ABBREVIATIONS

OF THE TITLES OF JOURNALS AND BOOKS.

Amer. Chem. J.	American Chemical Journal.
Amer. J. Pharm.	American Journal of Pharmacy.
Amer. J. Sci.	American Journal of Science.
Anal. Fis. Quim.	Anales de la Sociedad Española Fisica y Quimica.
Analyst	The Analyst.
Annalen	Annalen der Chemie (Justus Liebig).
Ann. Chim. anal.	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie.
Ann. Chim.	Annales de Chimie.
Ann. Falsif.	Annales des Falsifications.
Ann. Inst. Pasteur.	Annales de l'Institut Pasteur.
Ann. Physik.	Annalen der Physik.
Ann. Physique	Annales de Physique.
Annali Chim. Appl	Annali di Chimica Applicata.
Apoth. Zeit.	Apotheker-Zeitung.
Arch. Pharm.	Archiv der Pharmazie.
Atti R. Accad. Lincei	Atti della Reale Accademia dei Lincei.
Bentl. a. Trim.	Bentley and Trimen. Medicinal Plants.
Ber.	Berichte der Deutschen chemischen Gesellschaft.
Ber. Deut. pharm. Ges.	Berichte der Deutschen pharmazeutischen Gesellschaft.
Bied. Zentr.	Biedermann's Zentralblatt fur Agrikulturchemie und **rationellen** Landwirtschafts-Betrieb.
Bio-Chem. J.	The Bio-Chemical Journal.
Biochem. Zeitsch	Biochemische Zeitschrift.
Brewers J.	Brewer's Journal.
Bull. Imp. Inst.	Bulletin of the Imperial Institute.
Bull. Soc. chim.	Bulletin de la Société chimique de France.
Chem. Ind.	Chemische Industrie.
Chem. News	Chemical News.
Chem. Soc. Proc.	Journal of the Chemical Society of London. Proceedings.
Chem. Soc. Trans.	Journal of the Chemical Society of London. Transactions.
Chem. Weekblad	Chemisch Weekblad.
Chem. Zeit.	Chemiker Zeitung.
Chem Zentr.	Chemisches Zentralblatt.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Dingl. poly. J.	Dingler's polytechnisches Journal.
Färber-Zeit.	Färber-Zeitung.
Flück. a. Hanb.	Fluckiger and Hanbury. Pharmacographia.
Frdl.	Friedlander's Fortschritte der Teerfarbenfabrikation.
Gazz. chim. ital.	Gazzetta chimica italiana.
Helv. Chim. Acta	Helvetica Chimica Acta.
Jahrb. Min.	Neues Jahrbuch fur Mineralogie, Geologie und Palaeontologie.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Bd. Agric.	Journal of the Board of Agriculture.
J. Franklin Inst.	Journal of the Franklin Institute.
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry.
J. Inst. Brewing	Journal of the Institute of Brewing.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Phys. Chem.	Journal of Physical Chemistry.
J. pr. Chem.	Journal für praktische Chemie.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
J. Soc. Dyers.	Journal of the Society of Dyers and Colourists.
J. Tokyo Chem. Soc	Journal of the Tokyo Chemical Society.
J. Washington Acad. Sci.	Journal of the Washington Academy of Sciences.
Kolloid Zeitsch.	Kolloid-Zeitschrift.
Met & Chem. Eng.	Metallurgical and Chemical Engineering.
Min. Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Pharm. J.	Pharmaceutical Journal.
Pharm. Zeit.	Pharmaceutische Zeitung

Phil. Mag.	Philosophical Magazine (The London, Edinburgh and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society.
Phot. J.	Photographic Journal.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Proc. Roy. Soc. Edin.	Proceedings of the Royal Society of Edinburgh.
Rec. trav. chim.	Recueil des travaux chimiques des Pays-Bas et de la Belgique.
Trans. Faraday Soc.	Transactions of the Faraday Society.
Zeitsch. anal. Chem.	Zeitschrift für analytische Chemie.
Zeitsch. angew. Chem	Zeitschrift für angewandte Chemie.
Zeitsch. anorg. Chem	Zeitschrift für anorganische Chemie.
Zeitsch. Nahr. Genussm	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
Zeitsch. öffentl. Chem.	Zeitschrift für öffentliche Chemie.
Zeitsch. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Zeitsch. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.

A
DICTIONARY
OF
APPLIED CHEMISTRY.

EXPLOSIVES. Explosives are solid, liquid, or gaseous mixtures or chemical compounds, which by chemical action (set up in them locally by flame, by a blow, or by other means) generate suddenly large volumes of heated gas.

The rate at which the expansive force, which characterises an explosive reaction, is developed, varies considerably, and determines whether the reaction is a combustion, explosion, or detonation. These terms are purely relative, and there is no definite line of demarcation between them.

The factors determining the rapidity of an explosive reaction are the chemical nature of the explosive, its physical condition, the conditions under which it is exploded, and the method of firing.

The energetic action of an explosive largely depends on its rate of chemical change; in chemical compounds (like nitroglycerin and guncotton) the reacting atoms are in much greater proximity than are those of a mechanical mixture of solids (such as gunpowder), and in the former class the rapidity of the chemical action will be greater than in those of the latter class, composed of constituents by themselves non-explosive.

Nearly all the explosives in actual use are instances of oxidation, oxygen being supplied by a nitrate, by nitric acid, by an NO_2 group, or by a chlorate or perchlorate.

The oxidising compounds used in explosive mixtures and explosive compounds are frequently endothermic substances, the heat of decomposition contributing towards the expansion of the gaseous products of the explosion. The conditions for complete combustion of the combustible elements do not always give the maximum explosive effect; carbon burning to monoxide gives a larger evolution of gas, but less evolution of heat than on complete combustion, and the best composition for any given explosive effect has to be determined by experiment.

The physical condition of an explosive has a marked effect on its explosibility and the character of the explosion; frozen nitroglycerin is much less sensitive than the same explosive in the liquid state, nitro explosives that have been fused and cast are less sensitive to detonation than the same explosives in the crystalline or powdered condition, and the same gunpowder mixture gives various effects according to the size of the grain.

Confinement increases the effect of all explosives; the more rapid the explosive the less the confinement necessary to obtain its maximum effect. The power of mercury fulminate is but little increased by confinement, but explosives of the gunpowder type require to be strongly confined to produce disruptive effects.

An explosive reaction may be initiated by a heated solid, a flame, by friction, by percussion, an electric spark or current, or by the concussion from another explosion. The nature of the reaction is largely conditioned by the method of firing adopted; nitroglycerin or guncotton in contact with a flame burns quite quietly in the open, but when fired by the detonation of a small initial charge of mercury fulminate, the whole mass of the explosive decomposes practically instantaneously, and detonation results.

The various explosive reactions differ considerably in the amount of impulse necessary for their initiation. To have value as an explosive, a compound or mixture must not be too sensitive to impulse. Substances like nitrogen iodide and diazobenzene nitrate are too sensitive to have practical value. The most sensitive explosives in use, such as mercury fulminate and its mixtures, are used in small quantities in caps and detonators to initiate the explosion of larger masses of less sensitive explosives, propellants or high explosives.

The value of an explosive as a propellant or high explosive depends on its density, on the quantity of gas and heat liberated, and on the velocity of the explosive reaction. For a propellant the gas and heat evolution must be high: for a high explosive it is necessary that all the factors should have a high value.

Explosives may be classified either according to their chemical composition, into explosive

mixtures or explosive compounds; according to their effect and the purpose for which they are employed, into 'high' or 'low' explosives or 'disruptives' and 'propellants'; or according to the danger in handling, transporting, and storing them.

In this article, the chemical classificatiaon is adopted, as far as possible. All the substances having explosive properties are not included, but only those that have, or may have, value for practical purposes.

Explosive Mixtures.

In explosive mixtures, the combustible and supporter of combustion are present in separate ingredients, which are usually not in themselves explosive. The necessary speed of reaction is ensured by extremely fine subdivision and very thorough incorporation of the ingredients and by the oxygen being in a highly concentrated and more or less easily liberated form. An important characteristic of this class of explosives is that their effect may be varied by varying the proportions of the ingredients.

Explosive mixtures may be grouped, according to the source of their oxygen, into nitrate, chlorate, perchlorate, &c., mixtures. Only the mixtures of these oxidising substances with combustible ingredients, in themselves non-explosive, and those containing only a small proportion of an explosive compound added to improve the explosive properties of the mixture, will be considered under this heading. The mixtures of oxidising substances with explosive compounds, where the former are only of secondary importance, will be considered under the respective explosive compounds.

Nitrate Mixtures.

In the nitrates, the oxygen is in sufficiently strong combination to need a somewhat powerful disturbing agency to liberate it, so that the nitrate mixtures are not very sensitive and their action is comparatively slow.

Potassium nitrate mixtures.—Of the various nitrates used in explosive mixtures, the potassium salt is by far the best adapted for the purpose, and black powder, or gunpowder, is the most important member of this class of explosives.

Gunpowder.

Since the introduction of smokeless powders, gunpowder has been gradually superseded for most military purposes: both as a propellant and a disruptive it is obsolescent. It is still however, very largely used in industrial mining operations, as a propellant for sporting purposes, as a bursting or opening charge for shrapnel shell, and, the smaller sizes, for subsidiary military purposes, such as for primers and igniters for large smokeless-powder charges, for fuses, and as an ingredient in certain compositions.

Ordinary black gunpowder consists of an intimate mixture of potassium nitrate, sulphur, and charcoal. The composition of the black powder used for military purposes in different countries is given in the table below.

English black gunpowders contain about 1 to 1·3 p.c. moisture.

Manufacture.—A short account only of the process of manufacture will be given, mainly that used at the Royal Gunpowder Factory, Waltham Abbey.

The Ingredients.

The *nitre* employed at Waltham Abbey is wholly Indian nitre. As imported, the 'grough' saltpetre, as it is called, has been partially purified, but contains potassium and sodium chlorides, potassium, sodium, and calcium sulphates, sand, and organic matter; the total impurities averaging about 4½ p.c. It is submitted to a simple refining process, being first dissolved by heat in the water used for washing the purified nitre of a previous operation. The liquid is heated to boiling in large refining coppers, the scum on the surface being carefully skimmed off: the temperature of the liquid is allowed to fall to 104°, and it is then filtered through bags of coarse cloth into the crystallising vessels. The temperature of the solution on entering the crystallising vessels is about 88° to 82°, the liquid is kept in constant agitation with wooden hoes, whereby, as the liquid cools, fine crystals are formed. The solution is not stirred when its temperature is lower than 32°. If the solution were left to crystallise undisturbed, large crystals would form, and would enclose mother liquor. The crystals are drawn to the side of the crystalliser, and transferred to draining frames. The drained nitre flour then receives three washings with distilled water in quantities insufficient to dissolve the nitre, each washing is succeeded by draining; after the last washing the nitre is drained all night, and is removed (except the bottom part, which is very moist) to the store bins. After about three days in store it is ready for the

COMPOSITION OF BLACK POWDER USED FOR MILITARY PURPOSES.

—	Per 100 dry gunpowder		
	Potassium nitrate	Sulphur	Charcoal
England, Russia, Sweden, Italy, Turkey, United States	75·0	10·0	15·0
France, Belgium, Spain, Persia	75·0	12·5	12·5
Germany	74·0	10·0	16·0
Austria-Hungary	75·5	10·0	14·5
Portugal	75·7	10·7	13·6
Switzerland	76·0	10·0	14·0
Holland	70·0	14·0	16·0
China	61·5	15·5	23·0

powder manufacture, and contains from 3 to 5 p.c. of moisture, according to the season; the water is estimated and allowed for in weighing the charges.

The waters used for washing the crystals are employed for the solution of the crude nitre; the nitre is recovered from the crystallisation mother liquors by evaporation, and is treated as crude nitre.

From Désortiaux, it appears that the agitation of the solution of nitre during crystallisation in order to obtain fine crystals is in general use on the Continent; at least, he mentions it as in use at Lille, Wetteren, and Spandau. At the refineries at Lille, Wetteren, and Spandau, he states that glue is added to the boiling solution of the crude nitre (the weight of glue being about $\frac{1}{3000}$ that of the crude nitre); the glue coagulating and carrying down organic colouring matters. The process of purification was the invention of Béaume and Lavoisier, and existing processes follow theirs with slight modifications.

On the Continent, and by most private manufacturers in this country, "artificial' or 'conversion' saltpetre, or 'German saltpetre,' as it is frequently called, is almost exclusively used. It is made by dissolving 10 parts of sodium nitrate, 'Chile saltpetre,' and 9 parts of potassium chloride, obtained from Stassfurth 'carnallite,' in mother liquors from previous operations, concentrating and crystallisation. It is refined as above.

In 1894 Hellick discovered that 'German saltpetre' frequently contained notable quantities of perchlorate, and it was stated that several accidents in powder factories coincided with the presence of a considerable percentage of perchlorate in the powder. It was subsequently shown that powder containing perchlorate was not unduly sensitive. The perchlorate is, however, not uniformly distributed in nitre, but tends to agglomerate, and the irregular shooting obtained with some foreign sporting powders, as compared with English ones, has been attributed to the contained perchlorate.

The *sulphur* employed at Waltham Abbey is native Sicilian sulphur, of the best quality. In Sicily, the sulphur mineral is subjected to a liquation process, to separate the sulphur from the gangue. It still contains 3 to 4 p.c. gangue, from which it is freed by distillation. It is distilled from a large iron retort, provided with two tubes placed at right angles to each other; one tube (15 inches wide) communicates with a large dome-shaped subliming chamber, the other tube (5 inches wide) enters an iron pot which receives the distilled sulphur; this tube is jacketed for cooling with water. The tubes can be connected with the distilling vessel or cut off from it by means of valves. The distilling vessel receives its charge of sulphur, which is heated to boiling; during the earlier stages of the distillation the vapours are sent into the subliming chamber, where the sulphur condenses as 'flowers of sulphur'; later on the sulphur vapour is sent through the condenser, from which it runs into the receiver in the liquid form. It is allowed to cool somewhat, but not to its solidifying point, and is ladled into moist wooden moulds. Sulphur, of sufficient purity to be used in explosives without further treatment is now obtained in large quantities, by the 'Chance-Claus' process, from the calcium sulphide, which is the chief constituent of the residue formed in the manufacture of soda. Much of the sulphur used by private firms and abroad is also obtained from pyrites. The 'flowers of sulphur' are not used in the manufacture of the gunpowder, as they usually contain considerable quantities of sulphurous and sulphuric acids, but are redistilled.

The sulphur igniting in air at a low temperature—about 250°—renders the gunpowder inflammable, and, experience has shown, improves the keeping qualities of the powder. Under the influence of pressure in the manufacturing processes the sulphur flows and becomes colloidal, and cements the particles of the ingredients together. Sulphurless gunpowder is comparatively friable.

The *charcoal*. For making the charcoal for gunpowder, soft and light woods are chosen, as the charcoals they yield are more readily ignitable, of an average growth of from two to ten years. The wood should be cut in the spring, when it is in full vegetation, as then its bark can readily be removed; in the spring the tree is in fullest sap, but the sap is very watery, and contains but little salts in solution.

At Waltham Abbey, the woods used are: the alder buckthorn (*Rhamnus frangula*, L., improperly called dogwood), alder, and willow (*Salix alba*, L.). Dogwood charcoal is preferable for small-grain quick-burning powders; for powders of larger grain the slower alder and willow charcoals are used. The woods are grown in England, and are cut about four inches in diameter.

Désortiaux states that in France the so-called dogwood (*Rhamnus frangula*) is exclusively employed for making the charcoal for military and sporting powders; he states, however, that it is becoming increasingly difficult to procure, and that they are trying to replace it by willow, or by the wood of the spindle tree. In Germany, 'dogwood' (*R. frangula*), willow, and alder are used; in Russia, alder; in Austria, alder and hazel.

At Waltham Abbey, wood is usually kept for about three years, dogwood in thatched stacks, and willow and alder piled by cords in the open. By the method of carbonisation there followed, 25 p.c. of black charcoal should be obtained from the wood, rather more from dogwood. The wood is cut into three-feet lengths, which are split if differing much in thickness, and is packed into iron cylindrical cases called slips, 3 feet 6 inches long, and 2 feet 4 inches in diameter. The lid is fastened on, two openings (each about 4 inches in diameter) being left in the bottom of the slip. The slips are then placed in horizontal cylinders, the end of the slip with the openings going to the further end of the cylinder, in which end there are openings corresponding with those in the slips.

The cylinders are closed by tightly fitting iron doors, and are built into the wall, with furnaces underneath, so arranged as to admit of the accurate regulation of the heat throughout the operation of charring; this occupies with dogwood about 4 hours for R.F.G., and 8 hours for R.F.G.^{2} gunpowders. The flames surround the cylinder, the heat acting as nearly as possible on its whole surface. The gases and volatilised tar from the wood pass out through the openings in the slip and the corresponding holes in the retort, into pipes communicating with the furnace in which they are burnt; this saves a considerable amount of fuel. When the wood has been sufficiently charred, which is known by the violet colour of the flame from the burning gas, indicating the formation of carbonic oxide, the slip is withdrawn by means of tackling, placed in a large iron case or cooler, covered with a closely fitting lid, and allowed to remain until all the fire is extinguished, which takes about 4 hours; the charcoal is then emptied into smaller coolers, and sent to store. The charcoal is carefully picked over by hand, to ascertain that it all is properly and evenly burnt, and that no rivets from the slips have broken off. It is then kept from ten days to a fortnight in store before being ground, to obviate the danger from spontaneous combustion (caused by absorption of oxygen from the air) to which charcoal is liable when ground directly after burning.

The smaller the cylinders used, the more uniform is the composition of the charcoal produced, since so high a temperature is not needed to carry the heat to the centre of the charge; in the English powder mills, the tendency has been to use small cylinders, some of which hold only 77 lbs. of wood. The use of small cylinders, however, raises the cost of production (Désortiaux).

Violette states that, for the same temperature, a slow carbonisation gives a much higher yield of charcoal than a quick carbonisation; the percentage of carbon being also a little higher in the former case.

Instead of fixed carbonising cylinders, movable cylinders are now used in most black-powder factories. No 'slip' is used, but two cylinders are provided for each furnace, one being charged while a carbonisation is proceeding in the other. The charged cylinders are run into the furnace on rails, which support them over the fire. An elaborate arrangement for the regular distribution of the gases and products of distillation of the wood is used, by means of which they can at will be directed into any one of the furnaces or allowed partially to escape by the chimney.

The principal advantages claimed for this system are homogeneity of the charcoal, the ready regulation of the combustion of the gases by means of the distribution apparatus, and the cooling down of the charcoal out of contact with the air, which does away with the possibility of the charcoal taking fire.

In some English factories, vertical movable cylinders are used, the advantages being that a larger number can be fired at the same time, and the moving of the cylinders into the cooling room is greatly facilitated.

Böckmann mentions that some years ago the use of rotating cylinders was introduced in Sweden; the cylinders being turned 90° about their horizontal axes every half-hour during carbonisation. It is stated that a more uniform carbonisation is obtained, and fuel saved.

Violette, in 1848, introduced the carbonisation of wood by means of superheated steam. The steam was used at a pressure of ¼ to 1 atmosphere, and was raised to the required temperature by being passed through a worm of wrought-iron heated by a fire. For the production (from dogwood) of *charbon roux* containing 70 p.c. carbon, the temperature of the steam had to be about 280°: by using steam heated to about 350°, charcoal containing 77 p.c. carbon was produced, and by heating both cylinder and steam to a temperature not exceeding 450°, charcoal of 89 p.c. carbon was obtained. The charcoal produced by means of superheated steam is remarkably uniform in composition. The method, however, was abandoned, because it gave a larger yield of *charbon roux*, but not of black charcoal, than the ordinary method of carbonisation in cylinders; and the lightly-burnt charcoal was then only required for sporting powder. Also, the cost of production of the charcoal by the superheated steam apparatus was greater.

Guttler, in 1887, invented a process for carbonising wood, especially cuttings and pulp, straw, peat, &c., in heated CO_2. Carbon dioxide is stated to be preferable to superheated steam, on account of the moist state of the charcoal when cooled in the steam. Gases of combustion, as free as possible from oxygen, are actually used. A producer-furnace is arranged by the side of the charring furnace, in which the CO_2 is produced by blowing air through burning coke by means of a fan. The carbonic acid gas is then blown through a tube into the carbonising cylinder during the carbonising of the wood, &c., and the flow of CO_2 is maintained during the cooling, which in consequence of the presence of the gas may be very rapid.

Composition, &c., of the charcoal.—Carbonising the wood raises the percentage of carbon, diminishing the percentages of hydrogen and oxygen.

Désortiaux states that woods recently cut have almost the same percentage composition; the mean composition of the dried wood being 49·37 p.c. C, 6·14 p.c. H, 43·42 p.c. O and N, 1·07 p.c. ash.

Heintz gives the composition of alder wood *minus* ash, as 48·63 p.c. C, 5·94 p.c. H, 44·75 p.c. O, 0·68 p.c. N. Peterson and Schödler give alder wood *minus* ash as 49·20 p.c. C, 6·22 p.c. H, 44·58 p.c. O and N.

On heating, water, carbon monoxide, carbon dioxide, hydrogen, acetic acid, methyl alcohol, and tar are produced.

Violette found that dogwood was converted into slack-baked charcoal (*charbon roux*) at a temperature of 280°–300°; at 300° the yield (on the small scale) was about 34 p.c. and the composition of the charcoal was 73·24 p.c. C, 4·25 p.c. H, 21·94 p.c. O and N, 0·57 p.c. ash. Between 350° and 400°, black charcoals are produced, the yield being from 31 p.c. to 28 p.c., the composition ranging from about 77 p.c. to 81 p.c. C. Between 1000° and 1250°, the charcoal obtained was very black and hard, the yield was about 18 p.c., and the composition of the charcoal 82·0 p.c. C, 2·30 p.c. H, 14·10 p.c. O and N, 1·60 p.c. ash, at the lower temperature, and 88·14 p.c. C, 1·42 p.c. H, 9·24 p.c. O and N, 1·20 p.c. ash, at the higher temperature.

Experiments made at the Chemical Department of the War Department showed no great difference in the specific gravity of charcoals prepared from willow and alder at 394°–558°;

their specific gravity at 15·6° was 1·41 to 1·44. Willow charred at the maximum temperature of 394° for 9½ hours had the composition of 79·22 p.c. C, 4·02 p.c. H, 15·32 p.c. O and N, 1·44 p.c. ash, and specific gravity (at 15·6°) 1·414.

The higher the temperature of carbonisation, the less is the inflammability of the charcoal in air, and the greater the thermal conductivity. Violette states that the charcoals prepared from any kind of wood at 300° take fire when heated in the air to 360°–380°: the charcoals from light and porous woods burning more easily than those from hard and close woods. For the same wood he makes the following statement as to the relation between temperature of charring and that of inflammation in air:—

Temperature of charring	Temperature of inflammation.
260°–280°	340°–360°
290°–350°	360°–370°
432°	about 400°
1000°–1500°	600°–800°

The lightly-burnt charcoals are much more absorbent of water than those charred at a high temperature.

The charcoals used for the various kinds of Service black gunpowder range in composition from about 75 p.c. C to 86 p.c. C, according to the nature of the powder. All other conditions being the same (viz. proportion of KNO_3, S, and charcoal, size of powder, density, and moisture), the charcoal burnt at lower temperatures (having lower percentage of carbon) gives higher muzzle-velocities and pressures than charcoal burnt at higher temperatures and having higher percentage of carbon; that is, for gunpowder of the composition 75 p.c. nitre, 10 p.c. sulphur, and 15 p.c. charcoal. The greater inflammability of the lighter-burnt charcoal makes the gunpowder, of which it forms part, quicker-burning.

The wood is charred to expel moisture, which would lower the temperature of the explosion products of gunpowder, and to obtain a charcoal of suitable inflammability. Charcoal for large-grained powders should be jet-black in colour; for small-grained powders a more slackly burnt charcoal of brown-black colour is used. Before use the charcoal is hand-picked to remove any impurities and any portions insufficiently 'burned.'

Appended is a table of the percentage composition of some charcoals from gunpowders of Waltham Abbey make, and of a sporting powder, which will serve as types of the charcoal used in the different kinds of black gunpowder:—

—	W. A. Pebble	W. A. Rifle Large Grain	W. A. Rifle Fine Grain	W. A. Fine Grain	Curtis & Harvey Sporting.
C	85·26	80·32	75·72	77·88	77·36
H	2·98	3·08	3·70	3·37	3·77
O (and N)	10·16	14·75	18·84	17·60	16·62
Ash	1·60	1·85	1·74	1·15	2·25

(Noble and Abel, Phil. Trans. 1880, 171, 218)

Pulverising, mixing, and incorporating the ingredients.—At Waltham Abbey, the refined nitre is used for gunpowder without being previously dried or ground, but the moisture is estimated and allowed for. The charcoal is ground in a mill; the grinding is done by a cone working in a cylinder, both being suitably toothed. The ground charcoal is made to pass through a spout into a revolving reel of 32-mesh copper-wire gauze, 8½ feet long and 3 feet in diameter, inclined at an angle of about 4° to the horizontal, and making 38 revolutions per minute. The charcoal which passes through the gauze is fit for use, and is collected in a closed reel case; the charcoal too coarse to pass through the gauze falls through the further end of the reel into a vessel, and is reground. The sulphur is ground under a pair of iron edge runners, a smaller-sized incorporating mill, and is sifted through a reel similar to that used for the charcoal. Precautions are taken to connect the sulphur mill to earth, in order to allow the electricity generated by the rubbing of the sulphur to escape, and the machinery is not run rapidly. In some works the sulphur is mixed with a little nitre before grinding to prevent electrification. Besides the danger of ignition by a spark, the electrical charge causes the sulphur to ball together and interferes with the grinding.

The ground ingredients are carefully weighed out in their proper proportions; the largest charge worked in the incorporating mill is 80 lbs. The charge receives a preliminary mixing in the mixing machine, a cylindrical drum of gunmetal or copper, about 2 feet 9 inches in diameter and 1 foot 6 inches wide. An axle bearing 8 rows of gunmetal 'flyers' or fork-shaped arms passes through the centre of the drum; the drum and arms are made to revolve in opposite directions, the former making about 40 revolutions per minute, the latter 120. The mixing occupies five minutes, the mixture being then hand-sifted through an 8-mesh copper-wire sieve over a hopper, to remove foreign substances, which otherwise are liable to cause an ignition in the incorporating mill; the 'green charge' is then tied up in a bag ready for the incorporating mill.

The incorporating mill consists of a circular iron bed, about 7 feet in diameter, very firmly fixed in the floor of the building, on which two iron cylindrical edge runners revolve. The iron runners are 6½ feet in diameter, 15 inches wide, and weigh about four tons. They have a common axle resting in a solid cross-head attached to a vertical shaft, which passes through a bearing in the centre of the bed, and is in gear with the machinery.

The bed has a sloping outside rim. The runners are at an unequal distance from the axis, the eccentricity being equal to half the thickness of a runner; they thus work the charge in the inner and the outer part of the bed, their paths overlapping. The runners are followed by two 'ploughs' of wood, covered with leather, attached to the cross-head by arms; one plough works near the vertical shaft, the other near the rim of the bed, throwing the composition under the runners.

The green charge is spread evenly on the bed of the mill by means of a wooden rake; it is damp with the moisture of the nitre, but an additional quantity of distilled water (2 to 7 pints) is added from time to time, according to the state of the atmosphere; the moisture assists the incorporation, and the charge is kept not too dry or it would be scattered as dust, not too wet or it would slip away from the runners or cling to them.

The iron runners make 8 revolutions per minute, the green charge is worked under them for 4 hours for R.F.G. powder, for 7 to 8 hours for R.F.G.^{2} powder, and for 3 hours for R.L.G.^{2} and R.L.G.^{4}. Dust and reworked charges are worked for 40 minutes.

A drenching apparatus is placed over the bed of each mill, by means of which, in case of an explosion, a tank of water is overturned and the charge drowned. This is done by the action of the explosion gases on a flat wooden lever arrangement, pivoted, and attached to the tank. By means of a horizontal shaft connecting all the levers of a group of mills, an explosion in one mill drowns all the others.

The short radius of the circular path traversed by the runners causes them to take a twisting as well as a rolling motion, and gives them a combined crushing and grinding action very favourable to the thorough trituration and incorporation of the ingredients.

The 'mill-cake,' as the worked charge is called, should have a uniform appearance, and should contain 1 p.c. to 3 p.c. moisture for small-arm powders, 3 p.c. to 6 p.c. for the larger grained powders. Any 'mill-cake' left firmly caked on the bed is removed by wooden tools after thoroughly moistening. Many accidents have been caused through the use of metal tools.

Breaking down the mill-cake and pressing.—The mill-cake is next reduced to meal, for convenience in charging the press box, and in order that the powder may be uniformly pressed. The mill-cake is broken down by means of two pairs of gun-metal rollers, the upper pair being grooved and placed directly above the other pair, which are smooth. The rollers revolve towards each other, dangerous friction from the accidental presence of any hard substance being prevented by one roller of each pair working in sliding bearings connected with a weighted lever causing a pressure of about 56 lbs., so that the rollers would open at any greater pressure. The rollers are fed with mill-cake from a hopper (placed at one end of the machine, below the level of the upper pair of rollers), by means of an endless band of canvas 2½ feet wide, with cross strips of leather sewn on at intervals of about 4 inches. The band passes over a roller at the bottom of the hopper, and over another placed above the upper pair of rollers; on being set in motion it carries the cake from the hopper to a point from which it falls on to the first pair of rollers; the crushed cake then falls on to the second pair, by which it is reduced to meal. It falls into wooden boxes, and is transferred to a magazine ready for pressing.

The meal is pressed into cake by a hydraulic press, fed from an accumulator, the head and bed-plate of which are made of cast iron or cast steel. The powder is pressed between plates about 1 foot 8 inches by 2 feet 4 inches and about ⅜ inch thick. Formerly brass plates were used, but now ebonite plates are usually preferred, because they are not so easily bent out of shape, and also because they have sufficient elasticity to transmit the pressure evenly all over the layer of powder, even if they should get out of the horizontal. They have the disadvantage of becoming easily electrified; in fact, alternate layers of ebonite and powder really form an electric pile. To obviate any danger from the possible accumulation of electricity, the presses are provided with an earth connection.

In charging the press, a plate is first put on to the carriage, and round this is placed a wooden frame, deeper than the thickness of the plate. This frame is filled with powder, and the surface smoothed by means of a flat lath, and a second plate placed on the top. The frame is then lifted to the level of the second plate, and the process repeated until the whole charge is made up. A pressure of between 375 and 450 lbs. per square inch is applied, according to the fineness of the powder, the amount of moisture it contains, the state of the atmosphere, and the density required. The pressure is slowly applied, eased off and reapplied several times in order to obtain great density without using excessive pressures: the compression usually lasts from 30 to 40 minutes. A pressure of 375 lbs. per square inch applied for from 1½ to 2 hours produces a cake with an average density of 1·7 to 1·8. The centre of the cake has, however, a greater density than the edges; the edges of the cake are on that account cut away to the extent of about an inch. The amount cut away need not exceed 10 p.c. The centre layers of the pile are slightly less compressed than the top and bottom layers, but these differences in density are partly removed by the subsequent operations. The layers of pressed cake are broken into pieces with a wooden mallet and put into barrels.

Granulating or Corning.—The press-cake is converted into grain by means of a machine consisting of three or four horizontal pairs of gun-metal rollers in a gun-metal frame. The pairs of rollers are placed one above the other, on an axial line inclined at about 35° to the horizontal, the vertical distance between the pairs of rollers being about 2½ feet. For fine-grain powders, the highest pair of rollers has teeth ⅛ inch apart, the next pair has ¼ inch teeth, and the two bottom pairs have no teeth. Like those of the breaking-down machine, the rollers work in sliding counter-weighted bearings; they make about 25 revolutions per minute. The machine is fed with press-cake from a hopper by means of a moving endless band. Short screens, covered with copper-wire gauze (10-mesh for small arm powders), are placed under each pair of rollers except the bottom pair, so that the powder too large to pass through the gauze passes on from one pair of rollers to the next. Beneath the short screens are placed two long screens in an inclined position, the upper one of 10-mesh, and the lower one of 20-mesh copper gauze fixed in a frame. A rapid, longitudinal, vibratory motion is imparted to all the screens while the machine is working, to assist the sifting and the flow of the powder. The grain that passes through the short screens will fall through the 10-mesh long screen. That which is retained on the 20-mesh screen is R.F.G. or R.F.G^2 powder; it falls into boxes made to move forward as they are filled. The grains too large to pass through the short screens fall into separate boxes, and are transferred to the hopper to be passed again through the rollers; while the fine powder which passes through the 20-mesh sieve falls on to the wooden bottom of the frame and is collected separately, to be sent back to the incorporating mill for a short reworking.

For granulating R.L.G^2 and R.L.G^4 powders, three pairs of rollers are usually employed, the two upper pairs with larger teeth, the bottom pair smooth. The grain from the granulating machine is called 'foul grain.' By granulating a gunpowder there is no danger, as there would be with a dust, of segregation of the ingredients during transport according to their densities, the powder is less hygroscopic, there is less danger of escape from storing vessels, and the inflammability and rate of burning of the powder is increased, since the flame can penetrate more quickly through the charge.

Dusting and glazing.—R.F.G. and R.F.G^2. powders are freed from dust after granulation by being passed through a dusting-reel. This is a cylindrical frame about 8 feet long and 1½ feet in diameter, covered with 20-mesh copper-wire gauze, and set at a very small angle with the horizontal. The reel is enclosed in a case to catch the dust, but is open at both ends; it is fed continuously at the upper end with powder from a hopper, while the reel makes about 40 revolutions per minute. The powder falls from the lower end of the reel into barrels.

The polish given to the powder grains by glazing is of advantage in diminishing the tendency of the powder to absorb moisture, by breaking off any sharp angles and points, and stopping up the outer pores of the grain, and in enabling it to bear transport without going to dust. Glazing also increases the density of the powder: a powder with a density of, for example, 0·810 before glazing having its density progressively increased to 0·893 after 42 hours' glazing. The small-arm powders, R.F.G and R.F.G^2, are glazed in large drums - cylinders 2 feet wide and 6 feet in diameter (a pair of drums on one axle) making about 12 revolutions per minute. The drums each take about 900 lbs. of powder; they are run 5½ hours for R.F.G., and 10 hours for R.F.G^2. No graphite is used for these powders; the friction and heat caused by the motion suffice to produce a brilliant glaze. The glazed powder receives another dusting in a reel covered with 20-mesh wire-gauze, and is then sifted through an 11-mesh sieve into barrels. R.L.G^2 powder is run for 1½ hours in drums as above, with about one ounce of graphite per 100 lbs. powder. R.L.G^4 is glazed for 3 hours in the old pattern glazing barrels, the same proportion of graphite as for R.L.G^2 being added after the barrels have run for 2 hours. Each barrel takes about 400 lbs. of powder; they are 5 feet long by 2½ feet diameter of ends, and make 34 revolutions per minute. The graphite increases the gloss of the powder, and the powder is also rendered less hygroscopic through the increased density of the surface layer.

Stoving or drying, finishing, blending.—The next operation is drying, which is carried out in a drying-room heated by steam pipes. The gunpowder is placed in wooden frames about 3 feet × 1½ feet × 2½ inches with canvas bottoms, each holding about 12 lbs. of powder, and placed on open framework shelves with which the room is fitted, seven or eight tiers of shelves rising one above another, the steam pipes running under them. The moist air of the room is constantly changed by means of ventilators. At Waltham Abbey, about 50 cwts. of gunpowder are dried at one time. The time and temperature of drying vary with the kind of powder and the amount of moisture in it, the length of time and the temperature increasing with the size of the grain. Thus, R.F.G. requires 1 hour, and R.F.G^2 2 hours at 38°, R.L.G^2 2 hours at 43°, and R.L.G^4 6 hours at 46°. Another system of drying is to drive a current of cold air over steam-heated coils into the drying-room or stove by means of fans. In some factories, a current of cold air is used, after being freed from its moisture by means of calcium chloride, caustic lime, or strong sulphuric acid; and drying at ordinary temperatures *in vacuô* has also been tried. The drying should be done evenly and not too rapidly, so that the pores of the powder are not opened too quickly.

Rapid drying, too, has a tendency to cause the larger-grained powders to crack, and sometimes causes an efflorescence of nitre on the surface of the grains.

The dried powder is *finished* by being rotated in a horizontal reel—a long cylindrical wooden frame covered with canvas, making 45 revolutions per minute—the fine-grain being reeled longer than the large-grain powders. Finishing frees the powder grains from the small amount of dust produced in the process of drying, and gives them (and especially to small-arm powders) a final glaze.

Before drying, and again after finishing, a uniform blend or mixture is made of a large number of barrels of gunpowder. Advantage is taken of every opportunity, in the processes of the manufacture of gunpowder, to mix or 'blend' the grain together so as to obtain more uniform results at proof. This is done by means of a wooden hopper divided into four equal compartments, each able to hold a barrel of gunpowder; the compartments can be emptied simultaneously into a central shoot by means of openings with sliding shutters in the bottom of each. This method of blending, especially with the smaller sizes of grain, is found to give batches of powder with very uniform firing results.

Pebble and prismatic powder. These cut and moulded powders are no longer manufactured, as smokeless powder is now used even for guns of the largest calibre, but a short account of them is given, owing to their great historical interest. The use of pebble powder in this country dated from about the year 1865. Rodman had previously shown that in the gun the pressure diminished as the size of the grains of gunpowder increased, and that the velocity of the projectile could at the same time be maintained by an increased weight of charge.

Pebble powders (P, cubes of ⅝-inch; and P^2, 1½-inch cubes) were used for larger guns than were the rifle large grain powders. Up to the formation of the press cake, the processes of manufacture were, with some variations, the same as for the finer grained powders.

The *P powder* was cut from the press-cake, which was pressed into slabs of about 15 inches by 30 inches, and of the required thickness. The cutting machine consisted of two pairs of phosphor-bronze rollers, having longitudinal knife-edges with spaces between them corresponding to the required size of the powder. The first pair of rollers cut the press-cake into strips, which were fed on endless bands to the second pair of rollers, set at right angles to the first, which cut the strips into cubes. These cubes were allowed to fall into a dusting reel, with copper wire meshes but little smaller than the cubes.

P^2 powder was cut by hand from the press-cake by means of lever knives of gun metal—knives hinged at one end, with a handle at the other. The press cake was first cut into strips and then across into cubes.

Both P and P^2 powders were run in the glazing barrels, by which treatment the edges and corners of the cubes were rubbed down, and a harder surface produced. The powders were then dried at 51°, which required a very much longer time than for the smaller-grained powders; a finishing process followed, the powders being run in wooden barrels with ribs wide enough apart to combine sifting with the finishing glazing. A small quantity of graphite was introduced into the barrels towards the end of the finishing process.

Prismatic powder. This may be regarded as a modification of the perforated cake powder devised by Rodman in 1860. The latter powder consisted of cakes of powder compressed by the hydraulic press, of the diameter of the bore of the gun, and pierced longitudinally with holes of about ¼ inch diameter, the cakes being packed in the cartridge so that the holes should correspond. Rodman was led to introduce this form of powder by the consideration that, with solid grains of gunpowder, the surface undergoing combustion in the gun diminishes as the combustion proceeds, and that consequently the strain on the gun is greatest in the earlier stages of the combustion. In the case of the perforated cake gunpowder, as the combustion progressed in the longitudinal holes, the surface undergoing combustion increased. Rodman's theoretical views were confirmed by experiment, but the liability of the perforated cake powder to break up by carriage or when handled, led to its replacement by much smaller hexagonal prisms with one central cylindrical hole; the prisms used in this country were about 1 inch high, the distance between opposite sides of the hexagon about 1·37 inches, the central hole about 0·4 inch in diameter. They were used for heavy breech-loading guns, and were packed so as to form rigid cartridges.

The prisms were pressed from a moderately large-grained powder granulated from press-cake freed from dust in the ordinary way, but not glazed, and finally dried and blended. The increased density of the powder due to the compression delayed the burning and reduced the initial pressure in the gun.

Brown or cocoa gunpowder. The introduction of this powder was a great innovation in powder making, as it greatly improved the shooting of big guns and allowed the use of guns of still larger calibre than even the black prismatic powder. It was composed of 79 p.c. nitre, 3 p.c. sulphur, and 18 p.c. charcoal per 100 of dry powder, and contained ordinarily about 2 p.c. moisture. The 'charcoal' also was a very lightly baked material, the percentage of carbon contained in it being but little higher than that in the (dry) wood or straw from which it was made.

This powder was used for heavy breech-loading guns in the form of hexagonal prisms, having the same dimensions as the black prismatic powder. The rate of ignition and of combustion of the brown prismatic powder was slower than that of the black, and for equal muzzle velocities of the projectile it produced less pressure in the powder-chamber of the gun than black powder, and gave a thinner smoke than the latter. This was due to the fact that the brown charcoals flowed under the high manufacturing pressure and bound the ingredients into a non-porous mass; black prismatic powder was comparatively porous.

Brown or cocoa powder gives on explosion a greater quantity of heat and a smaller volume of permanent gases than does an equal weight of black gunpowder; but the larger amount of water vapour in the products of explosion of brown powder have an important influence in lowering temperature. The products of explosion of brown powder undergo considerable dissociation at first, thus lowering the initial pressure in the gun, and subsequent recombination, and so giving sustained pressures as the projectile moves along the bore. The more gradual development of the pressure and the reduction of the maximum pressure increased the life of the gun and rendered the use of lighter guns possible.

Sporting powder. Considerable quantities of black gunpowder are still used for sporting purposes. The proportions of the ingredients vary slightly from those used for military powders, in order to produce the desirable qualities of quick ignition and combustion. The ease of ignition of a black powder does not vary much with the composition, but an excess of charcoal quickens, whilst an excess of nitre slackens, the rate of combustion. To increase the rapidity of combustion, a slack-burnt or red charcoal is usually used instead of black. The composition of the sporting powder of several countries is given in the following table:—

Composition of Black Powder used for Sporting Purposes

	Potassium nitrate	Sulphur	Charcoal
England . .	75·0	10·0	15·0
France . .	78·0	10·0	12·0
Germany . .	78·0	10·0	12·0
Austria-Hungary	76·0	9·5	14·5
Switzerland .	78·0	9·0	13·0

The powders are of high grade and carefully made by processes practically identical with those used in the manufacture of military powders. Occasionally there are modifications, such, for instance, as the use of drums instead of mills for powdering and mixing the ingredients, because the charge can be less moist and the mixing more rapid, so that better incorporation results in a given time, with resultant greater regularity in shooting.

Mining and blasting powder. The chief requirements of blasting powder are that it should be cheap, slow burning, and develop as large as possible a quantity of gas at a high temperature. The usual composition of blasting powders in various countries is :—

Composition of Black Powder used for Mining and Blasting Purposes.

—	Potassium nitrate	Sulphur	Charcoal
England . .	75·0	10·0	15·0
France . .	72·0	13·0	15·0
Germany . .	70·0	14·0	16·0
Austria-Hungary	60·0	18·5	21·5
Italy . . .	70·0	18·0	12·0
Russia . .	66·6	16·7	16·7

These proportions are by no means rigidly adhered to. Thus, in England, blasting powders varying from the above proportions to - potassium nitrate 65, sulphur 20, charcoal 15, - are made, the proportion of nitre being diminished to make the mixture slower burning, an effect otherwise obtained by increasing the size of the grains or compressing to a higher density. Other compositions especially made for use in fiery mines will be mentioned later under 'Black powder safety explosives.'

Blasting powder is a large-grained powder, sometimes coated with graphite, compressed into cartridges by means of a hydraulic press. As will be mentioned further on, while the mining powder with low nitre and high sulphur gives on explosion a larger volume of permanent gases, it gives a much smaller quantity of heat than black gunpowder.

Fuse powder. A gunpowder of special quality and constant composition is now manufactured for use in 'safety' and other fuses. Formerly, siftings from mining powder were frequently used, but this caused unevenness in burning and was frequently the cause of accidents through 'hang-fires.' It is a mealed powder; that is, of very fine granulation, but free from dust.

Suitable mixtures, determined by trial, of slower and quicker burning powders are made to give the correct time of burning in the time-rings of shell fuzes.

Bickford's safety-fuse (Eng. Pat. 6159, 1831) is a time-fuse in the form of a flexible cord or cable which fits into the metal cases of the detonators used for initiating the explosion of cartridges or other masses of high explosive. It consists of a continuous and uniform train of specially prepared fine-grained powder enclosed in a covering of jute fibre, this core being contained in a tube of waterproof composition and tape, or sometimes, for use under water, in a metal tube. The rate of burning per unit length varies and is stated with the supply, and it is also liable to alter slightly on storage.

Properties and products of explosion.—The '*density*' (as determined by Bianchi's densimeter) of the different kinds of gunpowder mentioned ranges from about 1·67 in the case of R.L.G^2 to about 1·87 in the case of brown prismatic powder. Increase of density of a gunpowder causes its slower combustion, and (under comparable circumstances) diminishes the muzzle velocity of the projectile and the pressure in the gun.

Increase of the amount of moisture in a gunpowder causes diminished temperature of the products of explosion, and lessens the muzzle velocity of the projectile and the pressure in the gun.

Black gunpowder can be *ignited* by a blow or by an increase of temperature: it explodes at about 300°. The exploding temperature was taken by heating small grains of the gunpowder buried in the sand of a small deep sand-bath, in which the bulb of a Geissler pressure mercurial thermometer was immersed. Black prismatic gunpowder inflamed at about 290°, brown prismatic at 304°. At a temperature slightly above 100° the sulphur can be completely volatilised out of the powder without inflammation taking place. Violette determined the ignition point by projecting the powder on to molten tin kept at different temperatures. He found that all classes of gunpowder after powdering fired at from 265° to 270°, and that the firing point depends but little on the composition, but that the size and shape of the grain and the perfection of the incorporation affected the results; thus, blasting powder in grains fired at 270° and extra fine sporting powder at 320°.

The ignition of gunpowder is more difficult and the rate of combustion diminishes with diminished atmospheric pressure. In an atmosphere maintained at a pressure of about 0·5 inch mercury, gunpowder is not exploded by contact with a platinum wire heated to redness by an electric current; the grains in contact with the wire fuse, and, if the passage of the current be maintained, burn slowly without causing the explosion of the remainder. Under the high pressures produced in a gun when fired, the velocity of combustion of gunpowder very rapidly increases.

The *products of the combustion* of gunpowder have been examined by several chemists, of whom Gay-Lussac (1823), Chevreul (1825), Bunsen and Schischkoff (1857), Karolyi (1863), Federow (1868), Noble and Abel (1875–80), may be more particularly mentioned.

The investigation of the subject by Noble and Abel is much more complete than the others, and some of their results will be briefly mentioned.

The *quantity of heat* evolved by the explosion of gunpowder was determined by firing 10 to 20 grams of gunpowder in strong steel explosion vessels of 32 and 119 c.c. capacity respectively, the explosion vessels being surrounded by water in a calorimeter of the usual kind.

The *volume of permanent gases* produced was determined by exploding in closed steel vessels, having an internal capacity of about one litre, quantities of gunpowder varying in weight from about 100 to 800 grams. The vessels retained the whole of the products of explosion, and were provided with an arrangement by which the gases could be allowed to escape, and could be collected or measured. The pressure in the vessels was measured by means of the usual crusher gauge (piston acting on, and compressing, a small copper cylinder) contained in a plug screwed into the vessel.

The *pressures* in the explosion vessels varied with the density of charge $\left(\frac{\text{volume of powder}}{\text{capacity of vessel}}\right)$. With a density of charge of 0·3, the pressure observed was about 5 tons per square inch; with 0·7 density, the pressure was about 20 tons; with density 1, the pressure was about 42 tons; and with density 1·2, the pressure was about 56 tons.

The powders experimented with had the following percentage composition; the first three were of Waltham Abbey make:—

Nature of powder	Potassium nitrate	Potassium sulphate	Potassium chloride	Sulphur	Carbon	Hydrogen	Oxygen	Ash	Water
Pebble powder .	74·67	0·09	—	10·07	12·12	0·42	1·45	0·23	0·95
Rifled large grain R.L.G. . .	74·43	0·13		10·09	12·40	0·40	1·27	0·22	1·06
Fine grain . .	73·55	0·36		10·02	11·36	0·49	2·57	0·17	1·48
Sporting powder .	74·10	0·29	trace	10·37	10·66	0·52	2·29	0·31	1·17
Mining powder .	61·66	0·12	0·14	15·06	17·93	0·66	2·23	0·59	1·61
Spanish spherical powder . .	75·30	0·27	0·02	12·42	8·65	0·38	1·68	0·63	0·65
Cocoa powder .	78·83		—	2·04	Charcoal 17·80				1·33

The composition of the solid and gaseous products of the explosion of these gunpowders is given in the following table; the numbers given for the first three powders are the means of 9 experiments with density of charge from 0·1 to 0·9, the sporting and mining powders had density of charge 0·3, the Spanish spherical, 0·7:—

PERCENTAGE COMPOSITION BY VOLUME OF THE DRY PERMANENT GASES.

	Pebble	R.L.G.	Fine-grain	Sporting	Mining	Spanish spherical	Cocoa
Carbon dioxide . .	48·95	49·29	50·62	50·22	32·15	53·34	51·30
,, monoxide .	13·63	12·47	10·47	7·52	33·75	4·62	3·42
Nitrogen . . .	32·16	32·91	33·20	34·46	19·03	37·80	41·71
Hydrogen sulphide .	2·60	2·65	2·48	2·08	7·10	2·74	—
Methane . . .	0·31	0·43	0·19	2·46	2·73	—	0·31
Hydrogen . . .	2·35	2·19	2·96	3·26	5·24	1·29	3·26
Oxygen . . .	—	0·06	0·08	—	—	0·21	—

PERCENTAGE COMPOSITION BY WEIGHT OF THE DRY SOLID RESIDUE.

	Pebble	R.L.G.	Fine-grain	Sporting	Mining	Spanish spherical	Cocoa
Potassium carbonate . .	59·26	61·05	51·88	59·10	41·36	35·66	$KHCO_3$ 13·55 K_2CO_3 64·12
,, sulphate . .	12·93	15·10	22·71	21·65	0·59	48·55	22·33
,, monosulphide . .	18·98	14·46	18·16	12·42	37·10	7·72	none
Sulphur [1]	8·08	8·74	6·90	6·45	14·11	7·04	—
Potassium thiocyanate . .	0·25	0·22	0·13	—	2·95	0·04	—
,, nitrate . . .	0·24	0·27	0·17	0·29	0·09	0·95	trace
Ammonium sesqui-carbonate .	0·10	0·08	0·05	0·09	1·78	0·04	trace
Charcoal	0·16	0·08	—	—	2·02	—	—

The cocoa powder gives a completely oxidised saline residue, and the proportion of incompletely oxidised gases is smaller with this powder than with the others.

The quantity of heat (in gram-degree units), and the volume (at 0° and 760 mm.) of the permanent gases, per 1 gram of dry powder, were found by Noble and Abel to be:—

—	Units of heat	Cubic centimetres Permanent gases
Cocoa . .	837·0	198·0
Spanish spherical	767·3	234·2
Sporting . .	764·4	241·0
Fine-grain .	738·3	263·1
R.L.G. . .	725·7	274·2
Pebble . .	721·4	278·3
Mining . .	516·8	360·3

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[1] Present in the residue as higher sulphide of potassium.

It will be seen that the order of decrease of units of heat is that of increase of volume of permanent gases; and Noble and Abel observed that the products of heat-units by gas volume do not differ greatly from a constant value, that this points to the conclusion that the pressures at any given density of charge, and the power of doing work of the various powders, are not very materially different,—a conclusion verified by experiment for the three Waltham Abbey powders, and in a less degree also for the other powders. The total potential energy of gunpowder they estimated at about 340,000 kilogram-metres per 1 kgm. of powder, or a little under 500 foot-tons per 1 lb. This calculation supposes the infinite expansion of the products of combustion, but they estimated the actual energy of gunpowder realised by modern guns as varying from about one-tenth to one-fifth of the total theoretical effect.

The *temperature* produced by the explosion of gunpowder they estimated at about 2,100° in the case of the pebble or R.L.G. powder, at about 2,200° in that of the Spanish pellet powder (Noble and Abel, Trans. Roy. Soc. 1875, 1880; Nobel, Heat-Action of Explosives: a Lecture to Inst. Civil Eng. 1884).

Debus, in 1882, first showed that potassium disulphide is a product of the combustion of black powder. He considered that the combustion takes place in two stages, at first on oxidation, with the formation of potassium sulphate and carbonate, carbonic acid gas, free nitrogen, and, perhaps, carbonic oxide; and, secondly, a reduction in which free carbon and sulphur reduced the potassium sulphate and carbonate.

Debus also showed that from the percentage composition of the powders fired and the products of combustion, the combustion of the powder, as an end result, could be represented in the form of an ordinary equation, from which the theoretical work obtainable from the powder can be calculated (Debus, Annalen, vols 212, 213, 265, and 268).

Examination of gunpowder.—The powder, examined by the eye, should have a perfectly uniform colour, depending on its composition and a proper amount of glaze. Small white specks on the surface of the grains indicate that the nitre has effloresced during drying. The grains must be compact, not flat, in shape; and their size must be uniform, as tested by sifting; and free from dust, as shown by the powder leaving no mark on running it over a sheet of paper. The grains must be hard and crisp, as judged by crushing in the hand. The thoroughness of the incorporation is tested by 'flashing' a small measured quantity of the powder on a porcelain tile by means of a hot wire. The 'flash' should show but few sparks, and there should be no residual solid matter.

By the *density*, or *real density*, of a powder is understood the specific gravity of the grains or prisms, including the air contained in their pores. It is usually determined by the Bianchi densimeter. 100 grams of the sample, crushed, if necessary, but free from dust, are weighed out and transferred to the globe of the densimeter. This removable glass globe is fitted with stopcocks above and below, the upper is attached to an air-pump, the lower connected by means of a tube with a vessel of mercury, the density of which is known, at the temperature, usually 60°F. or 70°F., to which it is adjusted. The lower stopcock is closed, the globe exhausted, the stopcock opened, and the mercury then allowed to rise to the height which the atmosphere will support, the lower stopcock closed again, and the upper part of the apparatus opened to the air by means of the air-pump gauge stopcock. The operations are repeated, the mercury surrounding the powder grains being thus subjected to two atmospheres pressure. The globe is then closed, unscrewed, and weighed. Then if S = density of mercury at temperature of determination, W = weight of globe filled with mercury, and W_1 = weight of globe filled with powder and mercury: density of sample

$$= \frac{S \times 10}{(W - W_1) + 100}.$$

Hygrometric test.—All kinds of black powder are liable to absorb more or less moisture from the air, depending on the quality of their charcoal and saltpetre. The tendency any powder has to absorb moisture is determined by exposing it for a given time—24 hours for the smaller powders—in a specially insulated box at a recorded temperature, to air saturated with moisture, from a saturated solution of saltpetre. The increase in the weight of the powder, added to its previous moisture content, is taken as a measure of its 'hygrometric quality.' The results are, however, not very reliable.

Analysis.—*Moisture* is determined by loss, on the coarsely powdered sample, after 1 hour at 70°, or preferably by exposure over sulphuric acid until of constant weight.

The *nitre* is determined by extraction with warm water, filtering, and evaporating the solution in a platinum dish. The final washings should be kept separate, as the charcoal has a tendency to come through the filter, evaporated to dryness and again extracted, when the filtrate is clear and is added to the bulk. The nitre is dried at 280°, cooled and weighed.

The *sulphur* is estimated by heating 1 gram of powder in a beaker with strong nitric acid until the action moderates, cooling a little, adding a little potassium chlorate to complete the oxidation, and evaporating to dryness. The residue is treated with strong hydrochloric acid, and again evaporated to dryness. The residue is taken up with water (any insoluble matter, grit and graphite, being filtered off and weighed), and the solution precipitated with barium chloride, &c., as usual.

The *charcoal.*—The nitre is removed from the gunpowder by treatment with water, the charcoal and sulphur filtered off, dried, powdered, and treated with carbon disulphide to remove sulphur. The dried charcoal still retains a small quantity of sulphur, which is estimated by the method given above, after the charcoal has been dried in hydrogen in the same manner as for a combustion. The weight of sulphur is, of course, deducted from the weight of charcoal used for the combustion. About 0·5 gram of charcoal is taken for combustion; it is dried (in the boat in which it is to be burnt) by heating for 15 minutes to 170°, in the case of a black charcoal, in a current of hydrogen. The charcoal is allowed to cool in the current of hydrogen, and is transferred to an air-pump receiver, which is then exhausted. The boat with the charcoal is weighed in a closed tube. The combustion is made in oxygen, a length of granulated copper oxide, maintained at a red heat, being in front of the boat; and in front of the oxide of copper is a shorter length of lead chromate, heated to very low redness to absorb SO_2 or SO_3: in other respects, the combustion is made as usual.

Other Potassium Nitrate Mixtures.

Sulphurless gunpowder of various compositions has frequently been tried for special purposes, but without much success. Sulphur renders a powder easy of ignition and increases its rate of burning, and its inclusion is practically essential. Sulphurless powder, moreover, has a tendency to crumble to dust on storage or handling.

Antimony sulphide has been proposed as a substitute for sulphur in black powder, but it is only in certain detonating compositions that it is actually used.

Many combustible substances, amongst others coal, coke, peat, sawdust, bark, bran, tan, sugar, starch, dextrin, gum, hydrocarbons such as paraffin and naphthalene, ferro- and ferricyanides of potassium, tartaric acid, Rochelle salt, sodium acetate, &c., have been proposed and patented as substitutes for all or part of the charcoal in nitrate mixtures. Many of these substances are substituted in order to reduce the amount of smoke. They almost invariably reduce the inflammability of the powder, slacken its combustion, and leave a large amount of residue, but frequently give off larger quantities of gas. These mixtures were suggested principally as blasting explosives, and many were authorised for manufacture in this country, but at the present time their use is practically confined to the Continent.

A few of these explosives will suffice:

Fortis was a mixture of nitre, tan, and sulphur, with small quantities of iron sulphate and glycerol, and it was claimed that nitroglycerin was produced during explosion in a blast hole, with consequent increase of power.

Carbonite, as introduced by Hellhoff of Berlin, was a mixture of nitrobenzene, potassium nitrate, sulphur, and kieselguhr, said to be plastic enough to fill a bore hole, to be non-explosive by blows, when inflamed to burn away quietly without explosion, and when detonated to have the same explosive force as kieselguhr dynamite. It has been used in coal-mines in Germany, but modern carbonites contain nitroglycerin, and are mentioned under 'Dynamites.'

Carboazotine was a mixture of nitre, lampblack, sawdust, and sulphur, with a little iron sulphate. This explosive required compression into cartridges before it would explode.

Petrolite, as manufactured in Hungary, was a mixture of nitre, wood pulp, coke-dust, and sulphur.

Jahnite, as made in Austria, is a mixture of nitre, lignite coal, and sulphur, with very small quantities of picric acid, potassium chlorate, and calcined soda.

Amidogéne, a similar mixture to the last, contained nitre, charcoal, bran, or starch, and sulphur, with a little magnesium sulphate. This powder had a very slow rate of combustion, but developed large quantities of gas. It was used on a large scale for blasting operations at the Iron Gates on the Danube, and in coal-mines.*

Black Powder Safety Explosives.

Ordinary black gunpowder is unsuitable as a blasting agent for use in fiery mines, and its use is everywhere prohibited for this purpose. Many modifications of gunpowder have been tried, and several mixtures have been manufactured which were able to pass the official tests. A few of these mixtures are:

Argus powder, which contained 81 p.c. potassium nitrate, 18·5 p.c. charcoal, containing 30 p.c. of volatile matter, and 0·5 p.c. sulphur.

Earthquake powder, which contained 79 p.c. nitre, and 21 p.c. charcoal, containing 56 p.c. volatile matter.

Elephant-brand powders, which had the composition of ordinary gunpowder, but No. 1 was fired with 6 inches of ammonium oxalate, and No. 2 with 6 inches of sodium bicarbonate, in front of the cartridge.

Oxalate blasting powder, which was composed of 71 p.c. nitre, 14 p.c. charcoal, and 15 p.c. ammonium oxalate.

All these explosives were subsequently removed from the 'permitted' list.

Bobbinite, manufactured by Curtis and Harvey, is still on the 'permitted' list, and was the most extensively used of all safety explosives in this country in 1913. It is really a high grade gunpowder, containing but little sulphur, with added ingredients to increase the safety. As originally made, it consisted of 64 p.c. nitre, 2 p.c. sulphur, and 19 p.c. charcoal, with 15 p.c. of a mixture of ammonium sulphate and copper sulphate. In a later composition the mixture of ammonium and copper sulphates was replaced by 8 p.c. of starch and 3 p.c. of paraffin wax, the other ingredients being correspondingly increased. The mixture is compressed into pellets, which are coated with paraffin wax.

Bobbinite is safe to handle, and is fired without detonators; it is slow burning, and does not break up the coal so much as most safety explosives. A Home Office Committee was appointed in 1906 to investigate the alleged danger of 'bobbinite' in fiery mines, but it concluded that these fears were groundless, and the manufacture and use of the explosive was still permitted. The committee also concluded that the damage with 'bobbinite,' as with other explosives, was greater when the shots were not efficiently stemmed. It was the only powder of this class to pass the Woolwich test for 'Permitted Explosives,' but it afterwards failed in the more severe Rotherham test, and in 1914 its use was restricted to mines that were not fiery.

Sodium Nitrate Mixtures.

Sodium nitrate has a higher percentage of available oxygen than potassium nitrate, and is also cheaper, but its hygroscopicity is a great drawback to its use in powders intended for keeping a long time. In dry climates the sodium nitrate powders, made as required for consumption, have been used, as they effect a saving, and are more powerful than the corresponding nitre mixtures. A sodium nitrate mining powder was used, for instance, on a large scale and with considerable economy in the Suez Canal works; but such mixtures are not in very general use.

The replacement of the potassium nitrate of black gunpowder by an equivalent quantity of odium nitrate would give, according to Bertheot's calculation, if the chemical reactions were exactly the same in the two cases, a slightly greater quantity of heat and a larger volume of gases.

Mixtures containing sodium nitrate do not gnite so readily, and burn more slowly than hose containing the potassium salt.

The hygroscopic properties of sodium nitrate are chiefly due to traces of nitrates and chlorides of calcium and magnesium, which it is impossible o eliminate on a commercial scale; chemically pure sodium nitrate being only slightly deliquecent. In recent years, it has been proposed to add a small quantity of oil, or liquid, or molten olid hydrocarbon, to sodium nitrate explosives, n order to coat the particles of nitrate, and so prevent the absorption of moisture

Sodium nitrate has been used, or proposed, n mining powders, either alone or in partial ubstitution of the potassium nitrate, with practically all the numerous combustible subtances given under 'other potassium nitrate mixtures.' For example, one of the early forms of '*carbonite*,' made by Schmidt and Bichel of Schlebusch, consisted of 9-10 parts of sodium nitrate, 1 part of sulphuretted tar oil, and 0·5 part of nitrocumene.

Considerable quantities of sodium nitrate black blasting powder are used in the United States, an average composition being: 73 to 4 p.c. sodium nitrate, 16 p.c. charcoal, and 10 o 11 p.c. sulphur, and a mild explosive known as *sprengsalpeter*, which has the composition 75 p.c. sodium nitrate, 15 p.c. brown coal, and 10 p.c. sulphur, is largely used in the Stassfurth mines. Another German explosive of this class is called *Petroklastit* or *Holoklastit* It is a compressed mixture of 69 p.c. sodium nitrate, 5 p.c. potassium nitrate, 15 p.c. coal-tar pitch, 10 p.c. sulphur, and 1 p.c. potassium bichromate. It is more powerful, but less sensitive to blow, than ordinary gunpowder.

Barium Nitrate Mixtures.

Barium nitrate contains a smaller percentage of available oxygen than potassium nitrate, but, owing to its higher specific gravity, it contains more oxygen, bulk for bulk, than the latter salt, and from this point of view should be more valuable in disruptive explosives. It also has the advantage that it is the least hygroscopic of all the nitrates used in explosives, but its higher price is against its use. Explosives containing it have a higher ignition-point and are slower burning than those containing potassium nitrate.

Barium nitrate, mixed with gunpowder, was used at one time in Prussia for heavy guns, and a black powder containing barium nitrate, sulphur, and charcoal was also used. Wynants, in Belgium, introduced a gunpowder for military purposes, in which nitre was practically or wholly replaced by barium nitrate, the grains being dusted over with gunpowder to increase the inflammability. It was found to be unsuitable for small arms on account of its slow combustion, and for cannon, because of its 'fouling,' and was only used as a blasting powder.

Barium nitrate is chiefly used as a constituent in some modern military and sporting smokeless powders, but is occasionally suggested as the oxidising agent in blasting powders, for example, Easton (Eng. Pat. 18551, 1909) proposed a mixture of barium nitrate, trinitrotoluene, and aluminium powder for this purpose; and Burrows (U.S. Pat. 968919, 1910) specifies a mixture of 32 parts barium nitrate, 10 parts of toluene, and 8 parts of aluminium, with or without the addition of charcoal and paraffin wax. An English 'authorised' explosive named *Brockite* is a mixture of barium nitrate and aluminium powder.

Barium nitrate, however, is more usually found as a secondary oxidising constituent in explosive mixtures containing larger proportions of other oxygen salts. These are classified under the principal, or most characteristic, oxygen salt.

Ammonium Nitrate Mixtures.

In 1867 in Sweden, Ohlsson and Norrbin patented the use of ammonium nitrate alone as an explosive, and also of its mixtures with combustibles, such as charcoal, sawdust, naphthalene, nitrobenzene and picric acid, in proportions to give complete combustion. These mixtures were used to a limited extent for some time, but, owing to the hygroscopicity of the mixtures and the difficulty in ensuring their explosion, their use was dropped on the invention of blasting gelatine by Nobel.

Sprengel, in 1873, showed that a mixture of ammonium nitrate and lampblack or charcoal, mixed with ordinary sporting powder, when fired in a rifle, caused a considerable increase in the initial velocity of the bullet, as compared with the velocity imparted by the same weight of sporting powder (Chem. Soc. Proc. 1873, 805). Ammonium nitrate, although containing 60 p.c. oxygen, having a combustible base, has only 20 p.c. oxygen available for the oxidation of other substances: $NH_4NO_3 = N_2 + 2H_2O + O$; whilst potassium nitrate has 39·6 p.c. available oxygen, supposing K_2O to be formed. Ammonium nitrate melts at about 100°, and begins to decompose at 200°, undergoing what is practically an internal combustion. If heated suddenly to a high temperature, as by projecting it on a red-hot surface, it deflagrates violently, and De Bruyn, in 1891, showed that it can be detonated by the use of a sufficiently powerful detonator. The great drawback to the use of ammonium nitrate in explosive mixtures is that it is extremely hygroscopic.

An explosive powder for use in guns and for blasting purposes, patented by Gaens in 1885, and termed *amide powder*, is a mixture of ammonium and potassium nitrates with charcoal. The constituents were used in such proportions as to give, on ignition, potassamide KH_2N, in accordance with the equation:

$$KNO_3+NH_4NO_3+3C=KH_2N+H_2O+CO+2CO_2+2N_2$$

according to which the powder should be composed of 101 parts by weight potassium nitrate, 80 parts ammonium nitrate, and 40 parts charcoal. The potassamide is stated to be volatile at high temperatures, increasing the useful effect of the explosive, and burning without residue, It is claimed further for the *amide powder* that when burned it leaves very little residue, and gives much less smoke than ordinary gunpowder.

A so-called smokeless powder, known as '*Hebler powder*,' was at one time manufactured in Switzerland, and consisted of a mixture of nitre, ammonium nitrate, sulphur, and charcoal. It was practically non hygroscopic.

Not only does ammonium nitrate leave no solid residue on combustion, but its use in explosives has been found to greatly reduce the temperature of explosion, and this has caused it to be very largely employed in modern so called 'safety explosives' for use in fiery mines There are also a considerable number of ammonium nitrate explosives now in use for general blasting work, and the very large demand for shell high explosives during the last few years has led to the general use of ammonium nitrate mixtures with nitrohydrocarbons, especially with trinitrotoluene, for this purpose (*see* under, Trinitrotoluene) The increasing manufacture of nitric acid and ammonia by synthetic methods will probably lead to the use of this class of explosives being still further considerably extended. As above stated ammonium nitrate alone under sufficient impulse is an explosive, but it has been found that the addition of some combustible substance, not necessarily explosive in itself, is necessary to form an efficient blasting agent or military high explosive.

These explosives are used with thoroughly water-proofed wrappers, treated with paraffin, ceresin, and resin, crude vaseline, petroleum products, &c , or with wrappers of thin metal foil, and the particles of nitrate are frequently coated with similar substances, or with the other constituents of the mixture, from solution or by fusion, so as to render them non-hygroscopic. The addition to ammonium nitrate mixtures of several substances, such as semi solids made of glue, dextrin, &c , aniline metallic compounds, such as aniline copper sulphate, kieselguhr, &c., has been patented to counteract the action of atmospheric moisture, by absorbing any moisture originally present, or subsequently taken up on storage, and so leaving the explosive constituents in a dry state

In manufacture, the ammonium nitrate is roughly crushed if necessary, then thoroughly dried and powdered in a steam-jacketed edge-runner mill and sieved. The sieved nitrate is then intimately mixed in the same mill, or in a steam-jacketed pan with gunmetal stirrers, with the other ground and sieved ingredients. If a nitro-body of low melting point is a constituent of the mixture, it is usually added in the molten form, so as to coat and waterproof the grains of nitrate as far as possible. Finally the mixture is allowed to cool down to a certain extent, and then made up into cartridges and waterproofed, or packed for transport in metal-lined hermetically sealed packages. Ammonium nitrate undergoes a change of crystalline form at 32° with increase in volume, and its mixtures should not be made up into cartridges or packed at a higher temperature than this, or the cartridges exposed to the direct rays of the sun, as especially in the presence of a little moisture, they may set very hard and become extremely insensitive to detonation. In an atmosphere of less than a certain humidity ammonium nitrate is not hygroscopic, and wet ammonium nitrate will lose moisture and become quite dry again under these conditions, though deterioration of the explosive may have taken place whilst it was wet.

The ammonium nitrate mixtures are non-sensitive to shock, and require a strong detonator to ensure there is not a 'miss-fire,' and to detonate them completely and so develop their full force. Although the power of these mixtures is increased by compression, the difficulty of detonation also increases. Where increase in power is necessary, but the use of a more powerful detonator is undesirable, the difficulty of detonation may be overcome by using a small quantity of an intermediary 'priming' explosive, which frequently may be the original explosive itself in a loose form. The Soc Universelle d'Explosifs (Fr Pat 451754, 1912) claims that the ease of detonation of ammonium nitrate explosives is improved by adding an aqueous solution of gum with gunpowder in suspension to the granulated explosive Many of these mixtures are extremely difficult to ignite, and almost impossible to keep burning Le Chatelier has proposed to crystallise a little potassium chlorate with the ammonium nitrate to render the mixtures more sensitive Mere addition of the chlorate is inadmissible, because of the great danger in mixing, and the action of the mixtures is also somewhat irregular; the salts being isomorphous, they may be crystallised together in any proportions, and these difficulties overcome.

The following are some of the more important ammonium nitrate explosives, containing simple combustible substances :—

Cologne Rottweil contains 93 p c ammonium nitrate, 4 9 p.c. vegetable oil, 1 2 p c sulphur, and 0 9 p c. barium nitrate. This explosive is manufactured in this country under the name of *Pembrite*

Dahmenite at one time consisted of a mixture of the nitrates of potassium and ammonium with naphthalene. *Dahmenite A*, the modern variation, is composed of 91 3 p.c. ammonium nitrate, 6·5 p.c. naphthalene, and 2 2 p c. potassium dichromate. The naphthalene is melted with the nitrate, so as to coat and waterproof it.

Two Austrian safety explosives are *Dynammon*, containing 87-88 p.c. ammonium nitrate and 12-13 p.c. charcoal, and *wetter-dynammon*, which contains 94 p.c. ammonium nitrate, 2 p.c. potassium nitrate, and 4 p.c. charcoal.

Electronite, a 'permitted' safety explosive made by Curtis and Harvey at Tonbridge, is a mixture of 75 p.c. ammonium nitrate, and 5 p.c. barium nitrate with wood meal and starch. The products of detonation are chiefly water, nitrogen, and a little carbon dioxide, and the flame is of too low a temperature to fire explosive gas mixtures.

Electronite No. 2 consists of 95 p.c. of ammonium nitrate and 5 p.c. of wood meal and starch.

Fractorite contains 90 p.c. ammonium nitrate, 4 p.c. resin, 4 p.c. dextrin, and 2 p.c. potassium dichromate.

Progressite contains 89·1 p.c. ammonium nitrate, 4·7 p.c. aniline hydrochloride, 6 p.c.

ammonium sulphate, and 0·2 p.c. colouring matter.

Romite, a Swedish explosive invented by Sjöberg (Stockholm, Eng. Pat. 11658, 1887), was a mixture of ammonium nitrate mixed with a solid melted hydrocarbon (naphthalene, paraffin, and the like) gelatinised with a liquid hydrocarbon (such as paraffin oil), and contains pure or similarly gelatinised potassium chlorate. It was found to be unsafe, owing to the interaction between the nitrate and chlorate.

Westfalite is made by the Westphalisch-Anhaltische Sprengstoff-Actien-Gesellschaft. *No.* 1 contains 95 p.c. ammonium nitrate and 5 p.c. of resin or gum-lac. In *No* 2, 4 p.c. of the ammonium nitrate is replaced by nitre; and in *Westfalite improved*, 3 p.c. of ammonium nitrate is replaced by potassium dichromate. The ingredients are ground together with alcohol or other solvent of the resin, and then heated to drive out the solvent, ground further, and compressed into cartridges by a special shaking machine.

The nitro derivatives of the aromatic hydrocarbons, which, as a rule, are not in themselves explosive, form powerful explosives when mixed with ammonium nitrate.

Abelite is an English 'permitted' explosive of this class. Several varieties have been made. *No.* 1 contains ammonium nitrate, dinitrobenzene, and trinitrotoluene with sodium chloride as a moderant. *No.* 4 contains ammonium nitrate, trinitrotoluene, and starch, with sodium chloride.

The *Ammonites* are a class of explosives containing the nitronaphthalenes, manufactured by the Miners' Safety Explosives Co. As originally permitted it contained 88 p.c. ammonium nitrate and 12 p.c. dinitronaphthalene, but this was rendered safer by the addition of sodium chloride, the modified composition being 75 p.c. ammonium nitrate, 5 p.c. dinitronaphthalene, 20 p.c. sodium chloride, and up to 1 p.c. moisture. The charge is contained in a lead-tin alloy case, waterproofed with paraffin wax; limit charge 18 oz., pendulum swing 2·44 ins. *No.* 5 contained tri- instead of di-nitronaphthalene, and *No.* 4 had part of the ammonium nitrate replaced by sodium nitrate. The limit charge of *No.* 5 is 26 oz., and the pendulum swing 2·41 ins.

Amvis is a mixture of 90 p.c. ammonium nitrate, 5 p.c. wood meal, and 5 p.c. of chlorodinitrobenzene, or of a mixture of dinitrobenzene and chlorinated naphthalene.

Bellite, invented by Lamb, of Stockholm, is a mixture of ammonium nitrate with meta-dinitrobenzene. *No.* 1 contains 16·5 p.c., and *No.* 3, 7·5 p.c. of the nitrohydrocarbon.

The mixture is heated to a temperature of between 50° and 100°, in order to coat the particles of the nitrate with the fused nitro compound, and compressed into cartridges before the mixture is cold. In earlier mixtures, other nitrates were used, and the specification mentions other nitrohydrocarbons. Bellite is difficult to ignite, and ceases to burn if the source of heat is removed. It is claimed to be a very powerful and safe explosive for use in fiery mines, and can only be fired by a fulminate detonator.

As manufactured by the Lancashire Explosives Co., *Bellite No.* 1 contains 62–65 p.c. ammonium nitrate, 14–16 p.c. trinitrotoluene, 15·5–17·5 p.c. sodium chloride, 3·5–5·5 p.c. starch, and up to 2 p.c. moisture; limit charge 20 oz., pendulum swing 2·74 ins. Later varieties containing dinitrobenzene, which have passed the Rotherham test, are *No.* 2, containing 61 p.c. ammonium nitrate, 12 p.c. dinitrobenzene, and 27 p.c. sodium chloride; limit charge 32 oz., pendulum swing 2·42 ins.; and *No.* 4, containing 66 p.c. ammonium nitrate, 14 p.c. dinitrobenzene, and 20 p.c. sodium chloride; limit charge 18 oz., pendulum swing 2·92 ins.

Black Bellite contains 61 p.c. ammonium nitrate, 12 p.c. trinitrotoluene, 24 p.c. sodium chloride, and 3 p.c. plumbago; limit charge 30 oz., pendulum swing 2·48 ins.

The *Densites* are mining explosives of this class which have passed the Belgian tests for safety explosives. *No.* 3 contains 74 p.c. ammonium nitrate, 22 p.c. sodium nitrate, and 4 p.c. trinitrotoluene; limit charge 700 gms.; and *No.* 4 18 p.c. ammonium nitrate, 45·5 p.c. potassium nitrate, 19 p.c. trinitrotoluene, and 17·5 p.c. ammonium chloride; limit charge 850 gms.

Dorfit is a German explosive containing ammonium nitrate with 5 p.c. of potassium nitrate, the combustibles being trinitrotoluene and 4 p.c. flour, and some 15 to 20 p.c.; sodium chloride being added as restrainer.

Dreadnought powder on the English authorised list contains 73–77 p.c. ammonium nitrate, 14–17 p.c. sodium nitrate, 4–6 p.c. ammonium chloride, 3–5 p.c. trinitrotoluene, with up to 1 p.c. of moisture, and coloured with a trace of 'red oil;' limit charge 32 oz., pendulum swing 2·05 ins.; requires a *No.* 7 or more powerful detonator.

Faversham powder is a 'permitted' explosive, manufactured by the Cotton Powder Co. It consisted at one time of 85 p.c. ammonium nitrate, 11 p.c. dinitrobenzene, 1·5 p.c. ammonium chloride, and 2·5 p.c. sodium chloride; but more recent compositions are: *No.* 1, 84–86 p.c. ammonium nitrate, 10–12 p.c. trinitrotoluene, 1–2 p.c. ammonium chloride, 1–3 p.c. sodium chloride, and 0–2½ p.c. moisture; and *No.* 2, 87–93 p.c. ammonium nitrate, 9–11 p.c. dinitrotoluene, and 0–1 p.c. moisture. The explosive is contained in a metal case and fired by a No. 6 detonator. A later variety, compounded to meet the Rotherham test, contains 47·5 p.c. ammonium nitrate, 24 p.c. potassium nitrate, 10 p.c. trinitrotoluene, and 18·5 p.c. ammonium chloride; limit charge 24 oz., pendulum swing 2·61 ins.

Favier's explosive, the pioneer explosive of this class, first patented in 1883 by Favier of Paris, was a mixture of ammonium nitrate, mono-, di-, or trinitronaphthalene, and a little ammonium chloride, mixed and compressed whilst warm into metal cartridges, and coated with a solution of lac or resin. It was manufactured in England under the name of *Ammonite*, and by the French Government under the name of '*Explosifs N*' or '*Grisounites.*' Two explosives which have passed the Belgian tests are *Favier* 2 *bis*, containing 77·6 p.c. ammonium nitrate, 2·4 p.c. dinitronaphthalene, and 20 p.c. ammonium chloride; limit charge 500 gms.; and *Favier* 3 *bis*; containing 60 p.c. ammonium nitrate, 11 p.c. potassium nitrate, 8½ p.c. trinitrotoluene, 6 p.c. flour, 5 p.c. alum, 5 p.c. barium carbonate, 4 p.c. ammonium chloride, and 0·5 p.c. potassium permanganate; limit charge 750 gms

Fractorite B is an explosive on the Belgian permitted list. It contains 75 p.c. ammonium nitrate, 2·8 p.c. dinitronaphthalene, 2·2 p.c. ammonium oxalate, and 20 p.c. ammonium chloride; limit charge 450 gms.

Glückauf is a German ammonium nitrate safety explosive with wood meal as the principal combustible, but also contains 1 p.c. dinitrobenzene and 5 p.c. copper oxalate

The *Grisounites* are French explosives founded on Favier's patent. *Grisou-naphtalite-couche N1a* contains 95 p.c. ammonium nitrate and 5 p.c. trinitronaphthaline, and N4 is of similar composition, except that 5 p.c. of the ammonium nitrate is replaced by potassium nitrate. These two explosives, which have a theoretical temperature of explosion of not greater than 1500°, are used for coal getting, they are dyed green. *Grisou-naphtalite-roche N1b*, used for rock blasting, contains 91·5 p.c. ammonium nitrate and 8·5 p.c. dinitronaphthalene; it has a theoretical temperature of explosion of not greater than 1900°, and is dyed red. A variety, *N1c*, used in non-dangerous coal mines, contains 87·4 p.c. ammonium nitrate and 12·6 p.c. dinitronaphthalene, and is dyed yellow. *Grisou-tetrylite-couche* contains 88 p.c. ammonium nitrate, 5 p.c. potassium nitrate, and 7 p.c. 'tetryl.'

Kentite is an English permitted explosive containing 32–35 p.c. ammonium nitrate, 32–35 p.c. potassium nitrate, 16–18 p.c. ammonium chloride, 14–16 p.c. trinitrotoluene, and up to 2 p.c. moisture; limit charge 18 oz., pendulum swing 2·64 ins.

Minolite Antigrisouteuse is on the Belgian 'permitted' list. It contains 72 p.c. ammonium nitrate, 23 p.c. sodium nitrate, 3 p.c. trinitrotoluene, and 2 p.c. trinitronaphthalene; limit charge 400 gms.

Negro powder, as authorised for manufacture in this country, is a mixture of 86–90 p.c. ammonium nitrate, 9–11 p.c. trinitrotoluene, 1–3 p.c. graphite, 0–1 p.c. moisture, and a little colouring matter. The cartridges are wrapped in paraffined paper, and are fired by a No. 6 detonator.

Negro powder No. 2, which has passed the Rotherham test, contains 57 p.c. ammonium nitrate, 15 p.c. trinitrotoluene, 27·5 p.c. sodium chloride, and 0·5 p.c. graphite; limit charge 24 oz., pendulum swing 2·21 ins.

Neuwestfalit, a variety of Westfalit, containing nitrohydrocarbon, is on the German authorised list. It contains 70 p.c. ammonium nitrate, 11 p.c. dinitrotoluene, 2 p.c. flour, and 17 p.c. sodium chloride; limit charge 540 gms.

Nitroferrite contains 93 p.c. ammonium nitrate, 2 p.c. trinitronaphthalene, 2 p.c. potassium ferricyanide, and 3 p.c. of crystallised sugar.

Roburite, patented by Roth of Charlottenburg, in 1887 (Eng. Pat. 267*a*, 1887), had as a new feature the use of a chlorinated nitrohydrocarbon, chlorinated dinitrobenzene, said to render the explosive more sensitive, and also increase the dynamic effect, but all samples do not now contain this substance. Large quantities are manufactured in England near Wigan. No. 1 contains 87·5 p.c. ammonium nitrate, 7 p.c. dinitrobenzene, 5 p.c. ammonium sulphate, and 0·5 p.c. potassium permanganate, and *No.* 3 87 p.c. ammonium nitrate, 11 p.c. dinitrobenzene, and 2 p.c. chloronaphthalene. In later samples, trinitrotoluene is used in place of dinitrobenzene, with wood meal and potassium permanganate. *No* 4, which has passed the Rotherham test, contains 61 p.c. ammonium nitrate, 16 p.c. trinitrotoluene, and 23 p.c. sodium chloride; limit charge 18 oz., pendulum swing 2·86 ins.

Two German compositions that have passed the tests for safety explosives are *Roburit II* 2, containing 71·5 p.c. ammonium nitrate, 5 p.c. potassium nitrate, 12 p.c. trinitrotoluene, 6 p.c. flour, 5 p.c. sodium chloride, and 0·5 p.c. potassium permanganate, and *Roburit II.*, containing 55 p.c. ammonium nitate, 9·5 p.c. potassium nitrate, 12 p.c. trinitrotoluene, 6 p.c. flour, 7 p.c. sodium chloride, 5 p.c. ammonium chloride, 5 p.c. magnesite, and 0·5 p.c. potassium permanganate. The limit charge of the former is 350 gms., and of the latter 650 gms

The dried nitrate is incorporated with the molten nitro compound and compressed into cartridges as usual. Roburite has a brownish-yellow colour. It burns readily, but does not explode on burning. It is not sensitive to shock, friction, or pressure; it is practically flameless, and safe in fiery mines. It is more powerful than gunpowder, and its effect is not shattering.

Securite, a safety explosive invented by Schoneweg, in 1886, consists of 74–85 p.c. ammonium nitrate, and 15–26 p.c. metadinitrobenzene. Later varieties, called *Flameless securite*, also contain ammonium oxalate, and sometimes trinitrobenzene and trinitronaphthalene are used. The explosive is made by dissolving the salt in water, evaporating, drying at 80°, and adding the nitrohydrocarbon. The mixtures are coated with nitrated resin

Stamford powder, a permitted explosive, contains 68–72 p.c. ammonium nitrate, 21–23 p.c. sodium nitrate, 3–4 p.c. trinitrotoluene, 3·5–4·5 p.c. ammonium chloride, and up to 1 p.c. moisture; limit charge 12 oz., pendulum swing 2·12 ins

Thunderite contains 92 p.c. ammonium nitrate, 4 p.c. trinitrotoluene, and 4 p.c. flour.

Titanite No. 1 is a mixture of 85–88 p.c. ammonium nitrate, 6–8 p.c. trinitrotoluene, 4·5–6·5 p.c. charcoal dried at 100°, and 0–1 p.c. moisture.

Uplees powder contains 62–65 p.c. ammonium nitrate, 12·5–14·5 p.c. sodium nitrate, 4–6 p.c. trinitrotoluene, 13·5 p.c. ammonium chloride, 2–4 p.c. starch and up to 1·5 p.c. moisture; limit charge 16 oz., pendulum swing 2·64 ins.

Verstarktes chromammonit, reinforced chromammonite, is a modern German safety explosive containing 70 p.c. ammonium nitrate, 10 p.c. potassium nitrate, 12·5 p.c. trinitrotoluene, 7 p.c. chrome ammonium alum, and 6·5 p.c. vaseline.

Steele, in 1906 (Eng. Pat. 4115), proposed a mixture of 85 p.c. ammonium nitrate with 15 p.c. of nitrated resin, or a nitrated mixture of resin and starch; the latter is added in three successive portions, each portion being treated with atomised methylated spirit. The resin in this way is caused to coat the particles of nitrate and render them non-hygroscopic. In some cases 1–5 p.c. powdered aluminium may be added. A variety of this explosive called

Sterlite A, containing 2 p.c. castor oil, has been authorised in England.

Westfalite No. 3 contains 58–61 p.c. ammonium nitrate, 13–15 p.c. potassium nitrate, 4–6 p.c. trinitrotoluene, 20 22 p.c. ammonium chloride, and water up to 1 p.c.; limit charge 12 oz., pendulum swing 2·55 ins.

Withnell powder is a mixture of 88·92 p.c. ammonium nitrate, 4–6 p.c. trinitrotoluene, 4–6 p.c. dried flour, and 0–1·5 p.c. moisture. The explosive is contained in a water-proofed linen-paper wrapper, and fired by a No 7 detonator.

Ammonium nitrate mixtures with organic basic substances and their nitrates, such as aniline, guanidine nitrate, and urea nitrate, have been proposed. Kubin (Eng. Pat 11502, 1894) patented a mixture of 75 95 p.c. ammonium nitrate and 5–25 p.c. aniline or toluidine nitrate. The Carbonite Syndicate, Ltd., in the same year, proposed a mixture of 94 p.c. ammonium nitrate and 6 p.c. aniline hydrochloride, under the name of *Progressite.* Girard (Fr. Pat 350371, 1904) claims that a powerful explosive is formed by fusing together 80 parts ammonium nitrate and 88 parts guanidine nitrate

A class of ammonium nitrate safety explosives has come into use, in which a little nitroglycerin, sometimes gelatinised with soluble nitrocellulose, is added to overcome the insensitiveness of the mixture, but not containing enough of this constituent to place them amongst the dynamites Explosives of this type are:

Ammon-carbonit is composed of 80·3 p.c. ammonium nitrate, 5 p.c. potassium nitrate 6 p.c. coal dust, 4·5 p.c. powdered starch, 4 p.c. nitroglycerin, and 0·2 collodion cotton.

Donarit, which contains 80 p.c. ammonium nitrate, 12 p.c. trinitrotoluene, 4 p.c. flour, 3·8 p.c. nitroglycerin, and 0·2 p.c collodion cotton.

Melling powder contains 51 55 p.c. ammonium nitrate, 11–13 p.c. sodium nitrate, 5–7 p.c. trinitrotoluene, 3–5 p.c. wood meal, 4–6 p.c. nitroglycerin, 18–20 p.c. ammonium oxalate, and up to 2 p.c moisture; limit charge 12 oz., pendulum swing 2·62 ins

Super-Excellite consists of 73·5–77 p.c. ammonium nitrate, 6·5–8 p.c. potassium nitrate, 2–4 p.c. wood meal, 3·5–5 p.c. nitroglycerin, 9–11 p.c. ammonium oxalate, and up to 1·5 p.c. moisture; limit charge 10 oz., pendulum swing 2·74 ins.

Superite contains 80–84 p.c. ammonium nitrate, 9–11 p.c. potassium nitrate, 2 5 p.c. starch, 3·5–4·5 p.c. nitroglycerin, and up to 2 p.c. moisture; limit charge 10 oz., pendulum swing 2·53 ins.

Some ammonium nitrate mixtures are sensitised with nitrocelloluse instead of with nitroglycerin or nitroglycerin jelly. For example, the German Explosive *Fulmenit* contains 86·5 p.c. ammonium nitrate, 5·5 p.c. trinitrotoluene, 2·5 p.c. paraffin oil, 1·5 p.c. charcoal, and 4 p.c. guncotton. *Wetter Fulmenit* is of similar composition, except that 10 p.c. of the ammonium nitrate is replaced by sodium chloride, in order to reduce the temperature of explosion.

Monachit contains 12 p.c. trinitroxylene and 1 p.c. charcoal as combustibles, reinforced by 1 p.c. of collodion cotton.

Escales, of Munich, in 1899, first proposed the use of aluminium in an explosive, which was manufactured under the name of *Wenghœffer* (Eng. Pat. 24377), whilst in 1900 von Dahmen (Eng. Pat. 16277) claimed the use of aluminium, magnesium, or other light metal mixed with an oxidising agent, a suitable mixture suggested consisting of ammonium nitrate, aluminium, and charcoal in the proportions $4NH_4NO_3+2Al+C$. Subsequently, the charcoal was omitted, and an explosive suggested on the basis of the equation:

$$3NH_4NO_3+2Al = Al_2O_3+6H_2O+3N_2$$

That is, a mixture of ammonium nitrate and aluminium in proportions for the complete combustion of the latter would contain 81·6 p.c. ammonium nitrate and 18·4 p.c. aluminium. This mixture would yield 1578 calories per gram and evolve 682 c.c of gas. The charcoal is added to facilitate the detonation. Von Dahmen's explosive is now on the market under the name of *Ammonal*, and has given very good results, both as a mining explosive and as a high explosive for shells, the proportion of aluminium being varied according to the effect desired. The 'ammonal' permitted in this country as a mining explosive has the composition 93·97 p.c. ammonium nitrate, 4–6 p.c. aluminium, and 0–1 p.c. moisture, the explosive being contained in a thoroughly water-proofed case.

Ammonal B has the composition 94–96 p.c. ammonium nitrate, 2·5 3·5 p.c. aluminium, 2 3 p.c. wood charcoal, and 0–1 p.c. moisture. This explosive passed the Woolwich test. For ordinary blasting purposes a more powerful mixture is used, containing 72 p.c. ammonium nitrate, 25 p.c. aluminium, and 3 p.c. charcoal. These explosives are manufactured by the Roburite and Ammonal Co.

Ammonal is very insensitive, and burns with difficulty. It is said to be one of the safest explosives known. It is stable under dry conditions, but is hygroscopic under the conditions of humidity in which ammonium nitrate itself absorbs moisture. It is fired with the usual detonator, and the products of combustion are said to be harmless; they, however, contain a considerable proportion of carbon monoxide.

For an ammonal containing 72 p.c. ammonium nitrate, 23·5 p.c. aluminium, and 4·5 p.c. charcoal compressed to a density of 0·9, Bichel found the velocity of detonation to be 3450 m. per sec. The heat of explosion was 1600 calories, and the calculated explosion pressure was 9425 kg. per sq. cm. (Zeitsch. angew. Chem. 1905, 1889).

Ammonal has been used in this country for military purposes in bombs and grenades. In Austria four grades are manufactured containing 80–90 p.c. ammonium nitrate, 4–18 p.c. aluminium, and 2–6 p.c. charcoal, and it is a service explosive in that country.

Since the introduction of 'ammonal,' aluminium has been added as an ingredient in many other explosives, chiefly in mixtures of the ammonium nitrate class with nitrohydrocarbons. The aluminium is usually used in the form of powder, which is made by first pouring the molten metal into water, and then pounding the small irregular fragments so produced, after drying, under stamp-mills until a sufficiently fine powder is obtained. The use of aluminium and other easily oxidisable metals in the form of '*metal wool*,' has been patented, the fineness of division being said to exert a considerable influence on the force of the explosive.

The oxidation of the aluminium sets free a large amount of heat, and it is claimed that the mechanical effect of the explosives is considerably increased. Bichel, however (*l.c.*), contends that the results showing this increase have been obtained in the lead block test, and are fallacious, and that actual use in mines has demonstrated that the increase in efficiency due to the addition of aluminium is extremely slight. He affirms that aluminium can only be added economically to those explosives which have a low temperature of explosion; as with others, although there is some increase in the temperature of the explosion, it is more than counterbalanced by the decreased volume of gas produced. It has been found that the addition of a few per cents. of aluminium increases the rate of detonation of the explosives.

Macnab and the Ammonal Explosives Co., Ltd. (Eng. Pat. 16514, 1904) propose the addition of potassium dichromate to explosives of the 'ammonal' type. It is claimed that in this way more aluminium may be used, giving greater explosive power, without diminishing the safety of the explosive.

Ripping ammonal contains 84-87 p.c. ammonium nitrate, 7-9 p.c. aluminium, 2-3 p.c. charcoal, 3-4 p.c. potassium bichromate, and 0-1 p.c. moisture, and *St. Helen's powder* contains 92-95 p.c. ammonium nitrate, 2-3 p.c. aluminium powder, 3-5 p.c. trinitrotoluene and 0-1 p.c. moisture. Both these explosives passed the Woolwich tests. A more powerful variety for ordinary blasting purposes contains 47 p.c. ammonium nitrate, 22 p.c. aluminium, 30 p.c. trinitrotoluene and 1 p.c. charcoal. *Gesteins Westfalit B* and *C* are German ammonals containing dinitrobenzene and dinitrotoluene respectively.

Besides aluminium and magnesium, many other metals and similar substances which yield oxides reducible with difficulty, including copper, zinc, iron, silicon, ferro-silicon, silicon carbide, various alloys, calcium, boron, and such rare metals as those of the cerium group, have been proposed and patented for addition to explosive mixtures.

Sabulite is an ammonium nitrate explosive containing calcium silicide, with trinitrotoluene to help the detonation. It has been used in England for filling bombs and grenades, a usual formula being 78 p.c. ammonium nitrate, 14 p.c. calcium silicide and 8 p.c. trinitrotoluene. When loose this explosive has a density of about 0·8 and is compressed in cartridges to a density of 1·0 to 1·45 with consequent increase of efficiency, but if compressed beyond this it cannot be detonated satisfactorily. Segay (Eng. Pat. 113083, 1917) proposes to considerably increase the proportion of silicide, so that on explosion the products are not those of complete combustion, and states that the most powerful results are obtained when the proportions are such that the carbon is turned to carbon monoxide, and only half the hydrogen is turned to water. Suggested proportions are 66 p.c. ammonium nitrate, 27 p.c. calcium silicide and 7 p.c. trinitrotoluene. He claims that with this mixture the power is increased by 10 p.c. when loose, that the explosive can readily be detonated even when compressed to a density of 1·45, that it is less hygroscopic, and that it is more easily handled. The trinitrotoluene may be replaced by tetryl, tetranitraniline, hexanitrodiphenylamine, or nitroglycerin.

The metals may be mixed with other oxidising agents than ammonium nitrate, for instance, barium nitrate has been proposed in recent mixtures with aluminium. Adinau (U.S. Pat. 1056389) proposes a mixture of 69 p.c. barium nitrate, 29 p.c. trinitrotoluene and 2 p.c. lead chromate.

Lead nitrate has been proposed as the oxidising agent in explosive mixtures, together with the usual nitrohydrocarbons, or other explosive or semi-explosive compounds, for example, de Macar (Eng. Pat. 10456, 1900) proposes mixtures containing lead nitrate mixed with 17 p.c. dinitroxylene, 10 p.c. aminoazobenzene, or 45 p.c. dinitrocellulose. Ermel (Fr. Pat. 377509, 1907) claims that the addition of lead nitrate to ammonium nitrate explosives ensures certainty of detonation, the increased sensitiveness being counteracted by the addition of a small proportion of glycerol or liquid hydrocarbon.

Chlorate Mixtures.

The chlorates contain a large store of available oxygen, with which they part at a comparatively low temperature, and with combustible substances yield extremely brusque and violent explosives. Chlorates contain approximately the same percentage of available oxygen as the corresponding nitrates, but they form more sensitive and violent mixtures, owing to the fact that they are endothermic: the nitrates, with the exception of ammonium nitrate, are not. Berthelot (Mem. des Poudres et Salpêtre, 1900-1910) has shown that potassium chlorate alone can be made to detonate, by allowing a small drop of the fused salt to fall on a red-hot surface. Chlorate mixtures are readily exploded by friction or percussion, rendering their manufacture highly dangerous, and they are all liable to spontaneous ignition, if the ingredients contain, or are liable to generate, traces of acid. Mixtures with sulphur or a metallic sulphide are very sensitive, and are liable to become unstable. Traces of sulphurous and sulphuric acid present in the sulphur, or formed by oxidation on storage, liberate chloric acid which accelerates the oxidation and may ultimately lead to spontaneous ignition of the mixture. A further drawback to their use is that their sensitiveness to percussion and friction frequently increases on keeping and exposure alternately to moist and dry conditions,—a phenomenon that has been partly attributed to fine crystals of chlorate crystallising out on the surface of the mixture. The chlorates alone are liable to explode when suddenly heated to a high temperature: explosions have occurred when large quantities of potassium chlorate have been involved in fires.

Potassium chlorate mixtures. Berthollet, who discovered potassium chlorate in 1788, proposed its use as a substitute for nitre in explosive mixtures, but early experiments led to several serious accidents and temporary abandonment of its use. Since that time innumerable mixtures have been patented, usually with some attempt to counteract the extreme sensitiveness of the mixtures, by the addition of some deadening agent, such as an oil, vaseline or paraffin wax, to coat the grains of chlorate, or some special mechanical expedient, such as only mixing the chlorate and combustible immediately before use.

The usual combustible substances, sulphur, charcoal, peat, tan, sawdust, bran, starch, gum, sugar, and frequently potassium ferrocyanide and realgar, have been proposed, together with such deadeners as tar, pitch, paraffin, ozokerite, soap, glycerol, a syrup of grape sugar, boiled linseed oil, and indiarubber solution. The mixtures were frequently proposed to be used in a moist pasty condition.

Very few need be cited as examples. *White gunpowder* was a mixture of approximately two parts of potassium chlorate and one part each of potassium ferrocyanide and sugar. *Kinetite* was an explosive proposed by Petry, Fallenstein, and Lisch (Eng. Pat. 10986, 1884), consisting of potassium chlorate incorporated with nitrobenzene, thickened and gelatinised with a little collodion cotton and sulphur, as precipitated antimony sulphide. A modified 'kinetite' was made by omitting the antimony pentasulphide. It required a high temperature for ignition, and did not explode on heating. It was, however, very sensitive to friction and percussion, and so chemically unstable that its manufacture in this country was not authorised. Among foreign attempts may be mentioned *Petrofracteur*, favourably reported on by an Austrian military committee, consisting of 67 p.c. potassium chlorate, 20 p.c. potassium nitrate, 10 p.c. nitrobenzene, and 3 p.c. antimony sulphide; and Turpin's explosive, *Duplexite*, a mixture of 70 p.c. potassium chlorate, 10 p.c. charcoal, 10 p.c. dinitrobenzene, and 10 p.c. coal tar (Fr. Pat. 189426, 1888). In England, Kitchen (Eng. Pat. 11102, 1889) submitted a sample of explosive to the Home Office authorities, containing 3 parts potassium chlorate, 7 parts potassium nitrate, 7 parts sugar, and 1 part coal-dust and paraffin oil, that was favourably reported on, but was never put on the market; and practically the only chlorate mixture that was ever used, until some ten years ago, was *Asphaline* (Eng. Pat. 2488, 1881), which consisted of 54 p.c. potassium chlorate, 42 p.c. bran, and 4 p.c. nitre and potassium sulphate. The mixture was deadened with paraffin, ozokerite, or soap, and coloured pink with fuchsine. This explosive was manufactured at Llangollen, but it was not a practical success, owing to its bulky nature, and the licence for manufacture was subsequently withdrawn.

For many years no explosive containing potassium chlorate was licensed, and invention was turned in other directions, owing to the high cost of chlorate explosives, and the greater explosive power of such explosives as dynamite and guncotton. On the introduction of electrolytic potassium chlorate, the price was greatly reduced, and efforts were again made to obtain a practical chlorate explosive. The first electrolytic chlorate factory was started at Villers-sur-Hermes, in Switzerland, in 1889. It has not been found possible to make a satisfactory propellant with a chlorate mixture, as they are all too violent and uncontrollable, and explosives of this class that have had extended use are all detonating or blasting explosives.

Street, in 1897, invented *Cheddite* (Eng. Pat. 9970, 1897), the name being derived from Chedd in Switzerland, where it was first made. This explosive satisfied all tests, and is now very largely used as a blasting explosive. The composition of cheddite is constantly undergoing change in detail, but it is essentially a mixture of potassium chlorate with one or more nitrohydrocarbons and castor oil. Some examples are: *Type* 41, 80 p.c. potassium chlorate, 12 p.c. mononitronaphthalene, and 8 p.c. castor oil. *Type* 60, 80 p.c. potassium chlorate, 12 p.c. mononitronaphthalene, 6 p.c. castor oil, and 2 p.c. picric acid. *Type* 60 *bis*, 80 p.c. potassium chlorate, 13 p.c. mononitronaphthalene, 5 p.c. castor oil, and 2 p.c. dinitrotoluene. *Type* 60 *bis M*, 79 p.c. potassium chlorate, 15 p.c. dinitrotoluene, 5 p.c. castor oil, and 1 p.c. mononitronaphthalene. The cheddites of *Type* 60 are more violent than *Type* 41.

Colliery cheddite, as permitted for use in this country, has the composition 76·5–79·5 p.c. potassium chlorate, 14·5–15·5 p.c. mononitronaphthalene, 1·5–2·5 p.c. dinitrotoluene, 4·5–5·5 p.c. castor oil, and 0–1 p.c. moisture.

The method of manufacture of 'cheddites' is to heat the castor oil by steam, in a jacketed enamelled iron pan, to a temperature of 70°. The nitrohydrocarbon, or nitrohydrocarbons, are then added, and when the mass is molten and homogeneous, it is allowed to cool to 55°, when the warm and dry powdered chlorate is mixed in by means of a wooden spatula, and stirred until all white particles have disappeared. 25 kilos. of material can be made in about 7 minutes. Finally, the mixture is poured on to a wooden bench, allowed to cool to about 30°–35°, the mass being still somewhat plastic, and then crushed by rolling it with a wooden roller. The rolling process is repeated when the mass is cold. The finished explosive is in the form of brownish-white or yellow grains, but is sometimes artificially coloured.

The stability of 'cheddites' is said to be increased on prolonged storage. They are insensitive to shock and friction at ordinary and at very low temperatures, and burn more or less rapidly, without any tendency to explode even when fired in large masses. Keeping for a long period at 120° causes no decomposition. At 200° the oil decomposes, the nitro-compounds volatilise, and the mass dries and blackens; and they do not deflagrate until heated to the temperature of decomposition of the chlorate. 'Type 60' is said to be about as powerful in blast-holes as 'dynamite No. I,' although it only produces about half the effect of the dynamite in the lead-block test.

Deering, in 1905, found that a 'cheddite,' having the composition 73 p.c. potassium chlorate, 16 p.c. dinitrotoluene, 6 p.c. starch, and 5 p.c. castor oil, gave an explosive effect in a lead block=0·75, guncotton being unity, and that a thin layer between hardened steel surfaces required a blow of 120 foot-lbs. per sq. inch to cause slight charring in one part, whilst, with a blow of 160 foot-lbs. per sq. inch, the explosive practically all fired.

If incorrectly proportioned, the 'cheddites' are liable to exude oil on storage. They are readily compressible and their sensitiveness to detonation diminishes with increased density; care is, therefore, necessary to avoid over-ramming in use. The velocity of detonation increases with compression up to a certain point, but beyond this it rapidly diminishes.

Many explosives of the Street type have been introduced since 'cheddite,' various nitrohydrocarbons being combined with the chlorate. Improvements have been directed towards minimising the chance of exudation in hot climates. Street himself (Eng. Pat. 12760, 1898) proposed to use a sulphurated oil, fat, or fatty acid, made by heating the oils or fats with sulphur at 180° until they thicken, instead of ordinary oil. Girard (Eng. Pat. 214, 1900) thickened the oil with 10–15 p.c. hard or soft soap, and Bonnet (Zeitsch. angew. Chem. 1901, [44] 1120) displaced part or the whole of the oil by the free fatty acids. The French 'Explosif O4' is a mixture of 90 p.c. potassium chlorate and 10 p.c. paraffin wax; it has been used for military purposes. In O6 or 'minelite' the combustibles are a mineral oil residue and paraffin wax, and in 'Sébomite' they are tallow and nitrotoluene or dinitrobenzene.

Pyrodialite, introduced by Turpin in 1899, is prepared in two forms. First, Nos. 0 and I., explosives with flame, containing respectively 88 and 80 p.c. potassium chlorate, 5 and 6 p.c. vegetable charcoal, 10 and 18 p.c. neutral gas tar, and 3 and 4 p.c. sodium or ammonium di carbonate. Second, Nos. II and III., explosives without flame, in which about half the chlorate is replaced by sodium or potassium acetate, the other ingredients being approximately in the above proportions. Later, Turpin proposed the addition of 10–50 p.c. nitroglycerin to render these explosives more sensitive to detonation, and prepared similar explosives with ammonium perchlorate.

Ammonia nitrate powder is an explosive composed of 80 p.c. ammonium nitrate, 5 p.c. potassium chlorate, 10 p.c. nitroglucose, and 5 p.c. coal tar.

In 1908 a chlorate mixture called *Colliery Steelite*, consisting of 74 p.c. potassium chlorate, 25 p.c. so-called nitrated resin, and 1 p.c. castor oil, was licensed as a safety explosive. Steele (Eng. Pat. 22095, 1909) has proposed a safety explosive containing 85–97·5 p.c. potassium chlorate, 2·5–15 p.c. liquid vaseline of sp.gr. 0·885–0·80. *Kohlensilesia 4 A* is a German safety explosive containing 80 p.c. potassium chlorate, 16 p.c. resin, and 4 p.c. nitrated resin; a considerable proportion of sodium chloride is present in the 'safety' variety of this explosive.

The use with chlorate of explosive compounds like nitroglycerin and guncotton has also been patented. The nitrophenols form very sensitive mixtures with potassium chlorate, and ammonium salts should never be used in chlorate mixtures, owing to the possibility of the formation of ammonium chlorate on storage. Potassium chlorate is a constituent of nearly all detonating compositions, used as initial detonating agents for other explosives.

Other potassium chlorate explosives are mentioned under 'Sprengel Explosives.'

Other chlorates. Sodium chlorate is frequently substituted for the potassium salt in the various mixtures mentioned. For example, 'cheddites' are manufactured of the compositions *Type* 41*N*, 80 p.c. sodium chlorate, 12 p.c. nitronaphthalene, and 8 p.c. castor oil; *Type* 60*N*, 80 p.c. sodium chlorate, 13 p.c. nitronaphthalene, 2 p.c. dinitrotoluene, and 5 p.c. castor oil; and *Type O5*, 79 p.c. sodium chlorate, 16 p.c. dinitrotoluene, and 5 p.c. castor oil. These mixtures have very similar properties to those containing potassium chlorate: they are, however, liable to absorb moisture and the cartridges are consequently dipped in paraffin wax. They should not contain more than 1 p.c. moisture.

Barium chlorate has been proposed in a few mixtures, but its application is practically limited to pyrotechnic compositions.

Lead chlorate. Martin (Fr. Pat. 478351, 1915) suggests explosives made from basic lead chlorate by interaction with glycerin, sugar, dextrose, mannitol or tannin. Crystalline products are obtained which are used either alone or mixed with combustible materials.

Ammonium chlorate yields extremely powerful explosive mixtures, but on account of its instability, it has no practical value. It decomposes even at ordinary temperatures, and mixtures containing it are liable to spontaneous explosion. According to Gelhaar (Zeitsch. ges. Schiess u. Sprengstoffw. 1916, 166) a thin layer of the dried salt lost 80 p.c. of its weight in seven weeks, its nitrogen being partly oxidised to nitric acid, and violent decomposition took place after 11 hours at 40°, 45 minutes at 70°, or about 3 minutes at 100°. He also found that the dry salt was detonated by a weight of 2 kilos falling through a distance of 15 cm.

Perchlorate Mixtures.

Perchlorates contain a larger percentage of oxygen, and decompose at higher temperatures than the chlorates. Mixtures containing them are not only more powerful, but also much less sensitive to ignition, percussion, and friction, and consequently are safer to store and use than the corresponding chlorate mixtures. As with chlorates, the electrolytic production of these compounds, cheaply and in a pure state, has led to their largely increased use in recent years.

Potassium and *sodium perchlorate mixtures.* Formerly, potassium, and occasionally sodium, perchlorate was mainly used, combined with the usual combustible or explosive ingredients, but their use has now been almost entirely superseded by the ammonium salt. However, Trench (Eng. Pat. 8358, 1908) proposed the addition of 5–20 parts of potassium perchlorate to 100 parts of gunpowder to increase the strength and regularity of the explosive, and in the same year, Harris (Eng. Pat. 28012, 1908) suggests mining explosives, consisting of mixtures of potassium perchlorate and carbon with naphthalene and benzene, and other nitro derivatives in various proportions. Small proportions of paraffin oil and castor oil are also added.

M.B., or *Modified Black Powder, No.* 1, is a black gunpowder, used for blasting purposes, in which part of the potassium nitrate is replaced by potassium perchlorate. The potassium nitrate may be replaced by sodium or barium nitrate.

Chilworth Powders, No. 4 and No. 5, contain mixtures of potassium nitrate and perchlorate as oxidising agents, the combustibles being sulphur and charcoal, with the addition of a little flour in the former or paraffin wax in the latter.

A class of explosives called *Permonites* is made in Germany according to several formulæ, but all containing roughly equal parts of potassium perchlorate and ammonium nitrate as oxidising salts. The combustible constituents are trinitrotoluene, flour or starch, and wood meal; a little nitroglycerin, or nitroglycerin gelatinised with soluble nitrocellulose, is sometimes added to render the explosive more susceptible to detonation; and a mild form of the explosive contains a considerable proportion of sodium chloride.

Some varieties are: *Permonite I, or Gesteins Permonit*, 30 p.c. potassium perchlorate, 40 p.c. ammonium nitrate, 7 p.c. sodium nitrate, 15 p.c. trinitrotoluene, 4 p.c. flour, 3 p.c. wood meal and 1 p.c. of a jelly of gelatine in glycerine; *Permonite S.G.P.*, on the Belgian permitted list, 24·5 p.c. potassium perchlorate, 29 p.c. ammonium nitrate, 6 p.c. nitroglycerin, 7 p.c. trinitrotoluene, 4 p.c. flour, 3 p.c. wood meal, 1 p.c. of a jelly of gelatine in glycerine, and 25 p.c. sodium chloride; *Permonite*, as placed on the British authorised list, 31–34 p.c. potassium perchlorate, 39–43 p.c. ammonium nitrate, 3–4 p.c. nitroglycerin, 0·5–1 p.c. soluble nitrocellulose, 11–13 p.c. trinitrotoluene, 5–9 p.c. starch, 1·5–3·5 p.c. wood meal and 0–2·5 p.c. moisture. Permonite I. is more powerful, but also more sensitive to blow, than the S.G.P. variety.

Several explosives containing potassium perchlorate have passed the latest tests and have been placed on the British list of authorised explosives, but as these also contain a considerable proportion of gelatinised nitroglycerin they have been classified amongst the 'dynamites.'

Ammonium perchlorate mixtures. In 1898 Alvisi (Rev. prod. chim. 2, [6] 83, and Eng. Pat. 25838, 1898) proposed the use of ammonium perchlorate, then made from the sodium salt by double decomposition with ammonium nitrate, in explosive mixtures. He claimed that it increased the explosive and propulsive force of the mixture, as well as the ratio of the former to the latter. The ammonium perchlorate was substituted for the other oxidising salts in the proportion of their available oxygen, and sulphur or a metallic sulphide was added to counteract the insensitiveness to ignition or detonation, and he pointed out that the maximum effect of the mixtures is preferably obtained by the use of detonators themselves containing ammonium perchlorate. Ammonium perchlorate is stable at ordinary temperatures, but decomposes slowly at 145° according to the equation $NH_4ClO_4 = 2H_2O + N + Cl + O_2$.

Besides having a large percentage of available oxygen, ammonium perchlorate evolves a large amount of gas and heat on decomposition. It is endothermic, and has the advantage over the perchlorates of the fixed bases that its products of decomposition are entirely gaseous, but owing to the internal combustion of its hydrogen, it has less available oxygen. The decomposition is rapid and the velocity of the explosion wave is great. It can be detonated alone but only with great difficulty, and a very powerful detonator is necessary to give complete detonation. Its limit of sensitiveness to impact is represented by a weight of 5 kg. falling 50 cm.

It is non-hygroscopic and insensitive when pure; but the insensitiveness of the salt is greatly diminished if it contains even small quantities of ammonium chlorate. Admixture of ammonium perchlorate explosives with potassium or sodium chlorate in quantity is dangerous owing to the liability to the formation of unstable ammonium chlorate on storage, but the Aktiebolaget Carlit, Stockholm, has suggested (Eng. Pat. 112417, 1917) the presence of 0·005 to 1 p.c. of a chlorate other than ammonium chlorate to render ammonium perchlorate explosives more sensitive and increase their violence. Alvisi, later (Gazz. chim. ital. 31, i. 221), confirmed experimentally, by testing various mixtures with combustible and explosive substances, the theoretical advantages of ammonium perchlorate over all other oxidising salts, except ammonium chlorate; and Carbonelli (L'Ind. chim. 1910, 209) obtained equally favourable results.

Explosives containing ammonium perchlorate have the disadvantage of generating hydrochloric acid, and occasionally chlorine in the mine. This drawback is usually overcome by the addition of potassium or sodium nitrate, but manganese or its compounds, oxides, silicide, boride, manganate, or permanganate, have also been suggested for the same purpose.

Ammonium perchlorate is used in combination with the various combustible and explosive substances mentioned under the other oxidising salts. These mixtures are now established as powerful and safe explosives, and are largely used in England, the United States and on the Continent.

The ammonium perchlorate is manufactured from the electrolytically produced sodium salt, either by double decomposition with ammonium chloride or sulphate, or by the combined action of carbonic acid gas and ammonia on the solution. In the former process the sodium sulphate can be deposited in an anhydrous condition and free from perchlorate by evaporation of the mixed solutions under reduced pressure at from 60° to 85°C. (Aktiebolaget Carlit, Stockholm, Eng. Pat. 110544, 1917); the latter process has been patented by Given and the Atlas Powder Co. of U.S.A. (U.S. Pat. 1273477, 1918).

Yonck (Eng. Pat. 24511, 1903) suggested a series of safety mining explosives containing ammonium perchlorate, amongst which are: (1) 21·2 p.c. ammonium perchlorate, 37·3 p.c. sodium nitrate, and 11·5 p.c. naphthalene; (2) 37·4 p.c. ammonium perchlorate, 27·17 p.c. sodium nitrate, 8·34 p.c. ammonium nitrate, and 27·09 p.c. trinitronaphthalene; and (3) 48·4 p.c. ammonium perchlorate, 33·8 p.c. calcium oxalate, and 17·8 p.c. trinitrotoluene. Webster (Eng. Pat. 18622, 1909) proposed a mixture of 35 p.c. ammonium perchlorate, 45 p.c. sodium nitrate, 10 p.c. dinitrobenzene, and 10 p.c. sawdust, or the same mixture with 2 p.c. of the sawdust replaced by vaseline. Trench (Eng. Pat. 8358, 1908) proposed to increase the strength and regularity of gunpowder by the addition of from 5 to 20 p.c. of ammonium perchlorate.

Some 'cheddites,' containing ammonium

perchlorate are 'Type B,' 82 p.c. ammonium perchlorate, 13 p.c. dinitrotoluene, and 5 p.c. castor oil; and 'Type C,' 50 p.c. ammonium perchlorate, 30 p.c. sodium nitrate, 15 p.c. dinitrotoluene, and 5 p.c. castor oil.

Amanite is an English 'authorised' explosive, consisting essentially of ammonium perchlorate and myrabolans, usually with some sodium or potassium nitrate and a small quantity of agar-agar.

Blastine, manufactured by Marpal, Ltd., Cornwall, an English 'authorised' explosive that has been used in large quantities both for industrial and for military purposes. A usual composition is 60 p.c. ammonium perchlorate, 22 p.c. sodium nitrate, 11 p.c. dinitrotoluene, and 7 p.c. paraffin wax. In some varieties a little aluminium powder or alternately charcoal is used. It is in the form of soft yellow grains, which are readily compressed.

M.B. Powder, No. 2 is a mixture of ammonium perchlorate and sodium, potassium, or barium nitrate, with charcoal and sulphur as combustibles.

P.S.E. No. 15 is a mixture of ammonium perchlorate and rosin, and *shellite* is a mixture of ammonium perchlorate and paraffin wax.

The *Yonckites* are Belgian explosives of this class. *No.* 10 *bis*, on the Belgian authorised list, contains 25 p.c. ammonium perchlorate, 30 p.c. ammonium nitrate, 15 p.c. sodium nitrate, 10 p.c. trinitrotoluene, and 20 p.c. sodium chloride, the limit charge being 900 gms.; *No.* 13, a more violent mixture, contains 20 p.c. ammonium perchlorate, 27 p.c. ammonium nitrate, 27 p.c. sodium nitrate, 6 p.c. barium nitrate, and 20 p.c. trinitrotoluene.

Metals are used in mixtures suggested by Bowen (Eng. Pat. 21481, 1903) as a shell powder, 75 p.c. ammonium perchlorate, 12 p.c. aluminium, and 13 p.c. paraffin, and as a blasting powder, 72 p.c. ammonium perchlorate, 11 p.c. aluminium, and 17 p.c. nitronaphthalene; and by Palmer (Fr. Pat. 394833, 1908), in a mining powder, claimed to be non-hygroscopic, stable, powerful, and rapid, consisting of 50 p.c. ammonium perchlorate, 14 p.c. dinitrotoluene, 31 p.c. sodium or potassium nitrate, 5 p.c. aluminium powder, and 5 p.c. paraffin wax.

The Belgian explosive *Megadyne* is a mixture of ammonium perchlorate with aluminium powder and paraffin wax, and similar compositions, with or without the addition of wood meal, have been used for military purposes in this country. These explosives are cheap, easy to manufacture, safe to handle, permanent, and readily compressed; they do not explode, but only burn, when ignited, require a powerful detonator to detonate them, but are extremely powerful when their full power is brought out, and the rate of detonation is high for an explosive mixture (of the order of 4000 m. per sec.), so that they are locally violent. They must not, however, be too strongly compressed in use, or the rate of detonation, like that of the chlorate 'cheddites,' is lowered again.

Zinc powder has been suggested by Palmer and the Perchlorate Powder Co., Canada (Fr. Pat. 477678, 1915), in ammonium perchlorate explosives, which are stated to detonate readily and completely, and to have great stability. [illegible]

ammonium perchlorate, part of which may be substituted by the potassium salt, 10 p.c. zinc powder, 5 p.c. combustible carbon compounds, such as mineral jelly, and 3 p.c. of an asphaltic pitch or petroleum residue. If the last ingredient does not contain sulphur, this may be added up to 5 p.c. The ingredients are incorporated with alcohol and benzene, which are afterwards dried off. An explosive mixture of similar composition has been used for military purposes in England for bomb filling under the name of *Permite*.

Johnson and the Perchlorate Safety Explosive Co. (Eng. Pat. 14866, 1915, and 1480, 1916) claim mixtures of ammonium perchlorate, part of which may be replaced by the potassium salt, with 4 to 8, and 16 p.c. of rosin in different grades of the explosive. Other varieties contain zinc or aluminium, and mineral oil or wax may also be added. The explosive *Rexol* is of this type.

The use of silicon or a silicide, usually ferro-silicon, instead of a metal, as temperature raiser in this type of explosive has been suggested by the Stockholm Superfosfat Fabricks Aktiebolag, Sweden (Eng. Pat. 17583, 1915). The main combustible is either nitrated or un-nitrated naphthenes (rockoil residue of over 250° C. b.p.), or this together with the mixture of nitrotoluenes commercially known as 'liquid trinitrotoluene,' gelatinised by the addition of a little nitrocellulose, a little wood meal being also added to increase the speed of detonation. Two formulæ given are: (1) 74 p.c. ammonium perchlorate, 6 p.c. ferro-silicon, 18 p.c. rock oil residue, and 2 p.c. wood meal; (2) 74 p.c. ammonium perchlorate, 5 p.c. ferro-silicon, 10 p.c. gelatinised liquid trinitrotoluene, 9 p.c. nitrated rock oil residue, and 2 p.c. wood meal. The ferro-silicon is supposed to bind at least part of the chlorine in the residue; aluminium silicide is also suggested.

Mixtures of ammonium perchlorate with explosive compounds have also been proposed; for example, explosives compounded of ammonium perchlorate and nitroglycerin, with or without the addition of collodion cotton, and a detonating mixture with mercury fulminate, were suggested by Alvisi (Eng. Pat. 25838, 1898); and Luciani suggests the addition of guncotton to ammonium perchlorate mixtures, more especially with metals (Fr. Pat. 326037, 1902).

Other Oxidising Agents.

The permanganates of potassium and sodium, the dichromates of potassium and ammonium, and the peroxides of lead and manganese are all good oxidising substances, and are used to some extent in explosive mixtures, but usually in combination with the other salts, and need no separate mention. Potassium permanganate mixtures are frequently very sensitive. The utilisation of the expansive force of liquid air as an explosive has been described by Wood (Eng. Pat. 25025, 1902), and, more recently, liquid air and liquid oxygen have been suggested as the oxygen vehicle in explosives of the Sprengel type.

Sprengel Explosives.

Sprengel (Eng. Pat. 921 and 2642, 1871;

for blasting purposes, of a new class of explosives consisting of mixtures, made immediately before use, of an oxidising agent and combustible substance, in themselves non-explosive.

Some of these explosives are very powerful when detonated by means of mercury fulminate, and they have the advantage of being perfectly safe during storage and transport; but, seeing that they are really manufactured when the mixing takes place, their use in most countries would be forbidden, as this manufacture can only be authorised in a duly licensed factory. Further, they are difficult for a miner to manipulate with cleanliness and safety. In some modern Russian Sprengel explosives, the liquid combustible is contained in a vessel divided into separate compartments, so that separate portions of the cartridge are uniformly impregnated with separate portions of the liquid, with the result that the explosive action is more uniform.

Sprengel proposed mixtures of nitric acid of about 1·5 sp.gr. with nitrobenzene, naphthalene, nitronaphthalene, and picric acid, and of porous cakes of potassium chlorate with such combustible liquids as carbon disulphide, nitrobenzene, petroleum, and benzene, the mixtures being made in the proportions required for complete combustion.

Care has to be taken that the nitric acid does not get accidental access to the fulminate detonator, or premature explosion will occur.

By adopting the Sprengel principle, the use of chlorate explosives may be made reasonably safe, and considerable quantities have been used in the United States and on the continent. One objection to them is that, unless great care is taken in the dipping, variable quantities of liquid are absorbed and uneven effects and possibly partial detonation only may result. They are sometimes primed with gunpowder, and when this is the case precaution is necessary to avoid admixture of the gunpowder and chlorate.

Rackarock, as used in the United States in 1885 for blasting the Hellgate rocks at the entrance of New York Harbour, was a mixture of 79 p.c. powdered potassium chlorate, and 21 p.c. nitrobenzene, the chlorate contained in cotton cases being suspended in a wire cage from a spring balance and dipped in the liquid until the requisite weight was absorbed. These proportions were found by Abbot to give the maximum effect under water, the intensity of action being 108 p.c. of that of dynamite No. 1. '*Rackarock Special*' contains, in addition, from 12 to 16 p.c. of picric acid. Sometimes 'dead oil,' or a mixture of this, with nitrobenzene was used.

Rackarock has also been used in other important engineering work, in blasting the headings of the Vosburg Tunnel in Pennsylvania, and in works connected with the first Chinese railways.

Explosif O_3 or *Prométhée* is a French Sprengel explosive in which the liquid combustible is a mixture of nitrobenzene, turpentine, and naphtha in various proportions, but with the nitrobenzene as chief constituent, and the absorbent oxygen magazine is a mixture of potassium chlorate with a little manganese dioxide.

Wain (U.S. Pat. 1240272, 1917) suggests a Sprengel explosive of the chlorate type, the combustible liquid being a mixture of equal volumes of castor and raw linseed oils, with eight times their combined volume of petroleum, that has been submitted to a nitrating treatment with nitric acid. This liquid has a sp.gr. of 0·816, and is stated to be twice as readily absorbed in the chlorate as nitrobenzene.

Hellhoffite, introduced by Hellhoff of Berlin, was a mixture of dinitrobenzene and nitric acid. It was tried in shells; the two substances mixing during their flight or on impact. Suitably detonated, the mixture is a powerful explosive, more so than guncotton or ordinary dynamite.

Panclastite.—Turpin, under this name (Eng. Pat. 4544, 1881; and 1461, 1882), proposed the use of liquid nitrogen peroxide, a mixture of equal parts of carbon disulphide and nitrogen tetroxide, that is, $3CS_2+5NO_2$, being recommended as giving the maximum effect. The advantages of nitrogen tetroxide over nitric acid are its higher percentage of available oxygen, lower heat of formation, and absence of water, but the disadvantages in its use are obvious.

Oxonite, invented by Punshon (Eng. Pat. 2428, 1883), was a mixture of 46 p.c. picric acid and 54 p.c. nitric acid, sp.gr. 1·5, the acid being contained in the cartridge in a glass tube, which was broken just previously to use.

Donar is a Sprengel explosive invented by Fiedler (Eng. Pat. 8101 and 23284, 1901). The cartridge contains a compressed dry powdered mixture of potassium chlorate and potassium permanganate, with or without potassium dichromate, and a vessel containing a mixture of turpentine with nitrobenzene or phenol; the dry powder being saturated with the fluid shortly before use.

The Soc. Franç. des Poudres de Sûreté (Fr. Pat. 351289, 1905) proposes three combustible mixtures: (1) 27 p.c. orthonitrotoluene, 9 p.c. mononitronaphthalene, and 64 p.c. dinitronaphthalene; (2) 35 p.c. paraffin wax, 50 p.c. orthonitrotoluene, and 15 p.c. trinitro toluene; (3) 23 p.c. paraffin wax, 13 p.c. nitrotoluene, 13 p.c. trinitrotoluene, and 51 p.c. iron filings. These combustible mixtures are liquefied by warming to about 65°, and mixed with the oxygen yielding constituents, when required for use. A mixture of nitrates of ammonium, potassium, and aniline is used with (1), potassium chlorate with (2) and (3). Winand (Eng. Pat. 26261, 1907) has patented a mixture of tetranitromethane $C(NO_2)_4$, a liquid boiling at 126°, with petroleum and other carbonaceous matter. Tetranitromethane is a stable substance and only feebly explosive, but somewhat readily exploded by percussion. It dissolves paraffin and other hydrocarbons, forming a pasty mass. It contains 65 p.c. of available oxygen, and is exothermic.

Liquid air and liquid oxygen explosives.—Sprengel himself called attention to the possibilities of liquid oxygen, and pointed out that the beau ideal of a detonating explosive is a mixture of 8 parts, 88·9 p.c., of liquid oxygen, and 1 part, 11·1 p.c., of liquid hydrogen. The chemical affinities of oxygen in the liquid state are still strong, and a mixture of liquid oxygen with combustible matter, when initiated by a suitable detonator, forms powerful explosives.

Linde, in 1895, made practical use of the idea, and first used explosives in which liquid air was absorbed in cotton wool, wood charcoal, and other combustibles. These mixtures were found not to detonate very readily, and subsequently kieselguhr, petroleum charcoal, and cork charcoal were used as absorbents, sometimes with the addition of liquid petroleum; liquid oxygen was also tried. This improved the detonation, but the explosives were found to be unduly sensitive to blow. The porous case containing the absorbent was dipped in a vessel of liquid air for some time, and the cartridge was fired in the usual way by means of an electric detonator or Bickford fuse.

These explosives were patented under the name of *Oxyliquit*, and a full description of them is given by Sieder in the Zeitsch ges Schiess u. Sprengstoffwesen, 1906, 87. They were given an exhaustive trial by an Austrian Commission in 1899, and were largely used in blasting the Simplon Tunnel. Their cost is comparatively small, there is no danger in their manufacture, and they are powerful, but the practical difficulties in their use are great. The plant for producing the liquid air has to be close to the blasting operations, the liquid being transported in open cans, with consequent loss, the cartridges have to be fired within 5 to 15 minutes after preparation, according to their size, and the effect varies with the time of standing.

Schulz (Glückauf, 1898, 341) experimented with coal dust soaked in liquid air. He found that when the cartridges were dipped in liquid air of normal composition, containing 23·2 p.c. oxygen by weight, they were less powerful than ordinary dynamite, but were more powerful than dynamite if liquid air that had partly evaporated and contained 50 to 60 p.c. oxygen was used.

Furstenhoff (Fr. Pat. 377103, 1907) suggested an absorbent of powdered metal, such as aluminium or magnesium, the rapidity of explosion being increased by mixing the metals with hydroxides of calcium and sodium. The principle of keeping the liquid oxygen definitely apart from the combustible until the moment of use was introduced by Nodon (Fr. Pat. 448732, 1911). A thin brass cylinder containing the liquid oxygen was introduced into another double-walled brass cylinder with non-conducting material between the walls, surrounded by kieselguhr, saturated with a liquid carbon compound, such as alcohol, glycerin, benzene, or pitch, the cylinder of liquid oxygen being punctured immediately before the cartridge was fired. The Soc. L'air Liquide (Fr. Pats. 450750 and 451265, 1912) proposed an absorbing porous cylinder closed at one end, made of a mixture of kieselguhr with aluminium, or a metallic silicide or hydride, bound together by a little sodium silicate. The liquid oxygen being poured into the cylinder immediately before use, and in a later modification (Fr. Pat. 451265, 1912) substituted the aluminium by coal or a hydrocarbon.

Owing to the excessive military requirements of high explosives of a permanent character during the last few years, liquid air explosives have been largely used for industrial blasting work on the Continent. No new principles in their use have been enunciated, but the details have been the subject of several patents. Weber in Germany has suggested, for example, an absorbent of cotton, sawdust, powdered cork, or other combustible material, capable of absorbing more than its own weight of liquid air, the cartridge being reinforced by aluminium powder, or a mixture of this with magnesium, antimony, silicon, etc., in a separate container. For obtaining disruptive effects of a lower order, inert material, such as iron-ore dust, is substituted for part or all of the metal.

EXPLOSIVE COMPOUNDS.

In explosive compounds the combustibles, carbon and hydrogen, exist in infinitely close contact with oxygen in the same molecule. The most important compounds contain nitrogen in loose combination with all or part of the oxygen, so that the chemical equilibrium is more or less unstable. With the requisite exciting force the molecule undergoes more or less complete internal combustion, with almost instantaneous evolution of highly heated gaseous products. Explosive compounds are consequently, as a class, more sudden and violent in their action than the explosive mixtures, and it is evident that the nature of their explosion cannot be graded, as in these mixtures, by varying the ratio of combustible to oxygen.

The most important explosive compounds are produced by the nitration of organic compounds. They may be subdivided chemically into two main groups, the nitro derivatives and the true nitric esters, although technically they are all termed nitro explosives. Besides these two main groups, there are other classes of explosive compounds, such as the fulminates, amino, nitroamino, azo derivatives, azides, etc.

NITRO DERIVATIVES.

The nitro derivatives are, as a class, more stable and less energetic than the nitric esters. They are, unlike the nitric esters, not liable to spontaneous decomposition if slightly impure, and are stable even in the presence of relatively large quantities of acid. The difference in the explosive characteristics of the two classes is due to a lower percentage of oxygen, and consequent less complete combustion, and a more stable internal structure of the molecule in the nitro derivatives.

They are extremely difficult to explode by simple heating, although Berthelot has shown that even nitrobenzene may be exploded if a small quantity be dropped on to a highly heated surface, but they can all be exploded by the use of a sufficiently powerful detonator. Some of the higher derivatives, such as trinitrotoluene and trinitrophenol, are amongst the most powerful and important 'high' explosives known, but the lower derivatives are not explosives in themselves except under initiatory impulses impossible in practice, and are mostly used as constituents of explosive mixtures, principally with ammonium nitrate, potassium chlorate, or ammonium perchlorate, the nitrohydrocarbons being usually fused before mixing with the oxidising ingredient. Mixtures of nitro compounds are frequently used as explosives for specific purposes. The sensitiveness of trinitrotoluene may be increased, for example, by mixing with picric acid, and that of picric acid reduced by mixing with dinitrophenol.

Another advantage obtained by using such mixtures is that the mixtures melt and can be poured at a considerably lower temperature than the constituents. The eutectic mixture of picric acid and trinitrotoluene, containing about 34 p.c. of the former, melts at 55°.

Nitrohydrocarbons.

The hydrocarbons are nitrated in the usual manner by mixtures of nitric and sulphuric acids, the degree of nitration being controlled by the composition of the mixed acid, its proportion relative to the hydrocarbon, and the temperature of nitration. For the higher nitrations, 'oleum' or Nordhausen sulphuric acid is used for bringing up the concentration of the mixed acids, and when the nitration takes place in stages the spent acid from the higher nitration stage is frequently used, after adjustment of its composition for the first stage of the process. Economy of working is effected by the use of solid sodium nitrate instead of nitric acid in some cases.

The aromatic hydrocarbons used for the manufacture of nitro explosives are usually obtained by the fractionation of coal-tar, but some naturally occurring petroleums contain a considerable proportion of benzenoid hydrocarbons, and processes have been patented in the United States and in Germany for their production from petroleum and paraffin hydrocarbons by a process of 'cracking' and fractional distillation. The American Aetna Explosives Co. spent large sums in developing the U.S Bureau of Mines' vapour phase cracking process, but the cracked oil contained only about 3 p.c benzene and 2¼ p.c. toluene, and the best benzene and toluene obtained by fractionation contained about 10 p.c. of paraffins of the same boiling point. In the nitration of the toluene so obtained, for example, the mononitrotoluene first formed may be separated from the paraffins by solution in sulphuric acid before further nitration (Flürscheim, U.S Pat. 1225321, 1917).

The *nitrobenzenes* are not used as explosives alone, although they can be exploded with difficulty, but the mono- and di- derivatives are used, in combination with oxidising salts or with more explosive compounds, in many modern explosives mostly used for blasting purposes. Numerous instances of these are given. Dinitrobenzene is also used to some extent in some sporting semi-smokeless powders, and is added as a constituent in some dynamites to lower the freezing-point of the nitroglycerin and prevent freezing. Tri- and tetra-nitrobenzenes, obtained by the drastic treatment of benzene with mixed acids, are both more easily exploded than the di- derivatives, but little use has been made of them up to the present, owing to the difficulty in their manufacture and the poor yields obtained, although trinitrobenzene has been proposed as a substitute for picric acid as a high explosive by the Chemische Fabrik Griesheim (Ger. Pat. 79477, 1893). Trinitrobenzene is more powerful than trinitrotoluene. According to Dautriche (Mém. P. et Saltp. 1911–1912, 27) trinitrobenzene when compressed into pellets at pressures from 275 to 4125 kilos. per sq. cm. has a density of from 1·343 to 1·662. When loose its velocity of detonation is 3900 metres per sec., and in pellets at a density of about 1·3 a velocity of detonation of 6,700 metres per sec. 10 gms. exploded in a lead block gave an expansion of 241 c.c., that of trinitrotoluene being 216 c.c., and of picric acid 228 c.c.

Mono- and dinitro-benzene are active poisons, and care is necessary in handling bare explosives containing them as ingredients.

Nitrotoluenes.

The mono-, di-, and tri-nitrotoluenes are all, but principally the two latter, used as constituents of explosive mixtures, but the trinitro derivative has also become of importance as a high explosive for military purposes. Trinitrotoluene is obtained by the nitration of toluene in stages, so that it is unnecessary to make separate mention of the manufacture of dinitrotoluene.

The lower nitrotoluenes have toxic properties, and usually cause a very irritant dermatitis, although some persons are more or less immune from the latter. The poisonous character and irritant properties of crude trinitrotoluene are probably largely due to the lower nitro impurities, especially dinitrotoluene, but fatal cases of poisoning have been attributed to the presence of tetranitromethane.

Trinitrotoluene in the explosives industries of this country is usually known as 'T.N.T.,' and this was at one time the service name, but it is now called 'Trotyl.' It is also known in different countries under the names 'tolite,' 'trilit,' 'trinol,' 'tritolo,' and 'triton.'

Manufacture.—It is manufactured by the nitration in stages of the carefully purified hydrocarbon, about 99 p.c. pure and of about 0·866 sp.gr. The nitration is carried out usually in either two or three stages, in cast-iron vessels, sometimes enamelled. The nitrating pans are jacketed so that the temperature may be controlled by the circulation of either cold or warm water, and are provided with a suitable stirring apparatus, such as paddles and baffle plates, and usually with a cover through which pass a fume pipe, the acid supply pipe, a pipe for the hydrocarbon and a thermometer. The toluene is nitrated first of all to mononitrotoluene, or directly to dinitrotoluene in the two-stage method. In the first stage the waste acid from a previous tri-nitration is used after being brought up to the requisite strength by the addition of nitric acid, this being run into the toluene in some factories, in others the hydrocarbon is run into the mixed acid. A suitable acid mixture for mononitration is 170 parts of mixed acid, containing 2 parts of nitric acid of sp.gr. 1·42 and 3 parts of sulphuric acid of sp.gr. 1·84 per 100 parts by weight of toluene. The acid or hydrocarbon is run gradually and with constant agitation into the hydrocarbon or acid, the temperature not being allowed to rise above about 30°. When the admixture is complete and there is no tendency to further rise of temperature, the reaction is allowed to continue for about 30 minutes, the mixture allowed to separate, and the spent acid is drawn off. The crude mononitrotoluene is then converted into dinitrotoluene by treating 100 parts of the former with 215 parts of mixed acid, containing 1 part of nitric acid sp.gr. 1·5 and 2 parts of sulphuric acid of sp.gr. 1·84, the temperature during their slow admixture being about 60°.

to 70° and then raised gradually, with constant agitation of the mixture, to 90° to 100° and kept at this temperature for 30 minutes. The stirring is then stopped, the mixture allowed to settle, and the spent acid drawn off. The trinitration is effected by heating 100 parts of the crude dinitro product with 225 parts of oleum, containing 20 p.c. SO_3, and 65 parts of nitric acid of sp.gr. 1·5, first for 1 hour at 95° and then for 1½ hours at 120° C. After standing for some time, the spent acid is drawn off and the trinitrotoluene washed with water. A yield of some 80 to 85 p.c. of the theoretical is obtained.

It is advisable to carry out the nitration of the dinitro into the trinitro product as a separate operation, otherwise a very large volume of strong mixed acids at a high temperature is required, and this leads to a low yield owing both to the solubility of the product in the mixed acid, and to its partial oxidation. The manufacture of trinitrotoluene by one continuous process has, however, been considerably improved and is now frequently used. Will (Ber. 1914, 707) states that trinitrobenzoic acid and tetranitromethane may occur among the products of nitration, the latter, if present, being readily recognisable by its powerful and characteristic odour, and Capisarow (Chem. News, 1915, 247) states that the oxidising action of the nitrating acids is increased by the presence of metallic salts, sodium nitrate, and especially ammonium nitrate. Phenolic compounds are liable to be formed by the action of hydrogen liberated by the action of acid on the metal nitrating vessels, and sulphonic acids may occur if there is any deficiency of nitric acid in the mixed acids.

The waste acids of the early nitrations contain trinitrotoluene and other nitro products, which may be separated by dilution with water, or removed by agitation with solvents, before the acid is denitrated and concentrated. Leitch (Eng. Pat. 15455, 1915) uses toluene or mononitrotoluene for the extraction, under suitable conditions of temperature and concentration, the product being again submitted to the nitration processes, and Johnson (U.S. Pat. 1271578, 1918) submits the spent acid to reduced pressure, the liberated gas bubbles float the trinitrotoluene to the surface and the spent acid is drawn off from below.

Purification.—The crude trinitrotoluene, which melts at about 70°, is washed free from acid by melting and repeated agitation with hot water, sometimes made alkaline in the early washes with a little caustic or carbonate of soda. Purification by washing with alkali is inadvisable, however, for Will has shown (Ber. 1914, 711) that dinitrocresylates are formed from the β and γ trinitrotoluenes present as impurities by the action of alkalies, which like the nitrophenates are sensitive salts. After drying the product forms commercial *crude trinitrotoluene*, and is used of this purity for most commercial explosive mixtures and for many military purposes. It consists essentially of symmetrical α, or 2.4.6 trinitrotoluene, with small quantities of the β or 2.3.4, and γ or 2.4.5 trinitrotoluenes with some dinitrotoluene and possibly mononitrotoluene. In addition, besides traces of the impurities mentioned above, free acid and sometimes alkali, may be present.

For some purposes the crude trinitrotoluene is further purified either by soaking the powder in a solvent such as cold alcohol or benzene, in which the impurities are more soluble, or by recrystallisation from the same solvents, or preferably a mixture of the two is used containing 10 p.c. benzene, or from light petroleum or toluene. Recrystallisation from mononitrotoluene has been patented by Roberts and Stuart (Eng. Pat. 7047, 1915), the solution of impurities being used for further manufacture of trinitrotoluene, but freeing the product from mononitrotoluene must be difficult, and in France recrystallisation from strong sulphuric acid is sometimes used, with subsequent washing with water. In recrystallisation from alcohol, or alcohol and benzene, the crude trinitrotoluene is dissolved in a steam-jacketed vessel fitted with a condenser, the solution sucked through a filter cloth by a vacuum, and the trinitrotoluene allowed to crystallise out. A second recrystallisation may be used where a product of the highest degree of purity is required. The crystals are freed from residual solvent first by whizzing in a centrifugal and then by exposing on trays in drying ovens heated by hot air, or sometimes the product is dried more quickly in the molten condition in vacuum driers, and afterwards cast and powdered.

Specifications.—The following specifications for the two grades of trinitrotoluene issued by the U.S. Navy Department are typical:—

Grade A. Refined.—The trinitrotoluol must be a high-grade material, made from a suitable quality of raw materials. It must be thoroughly purified by recrystallisation from an approved solvent, so that the finished product shall have the following characteristics. The material must be in the form of a slightly yellow, fine, and uniform crystalline powder. At least 99 p.c. must pass through a sieve of 12 mesh to the linear inch. No odour of any by-product or crystallising agent may be present. It shall have a m.p. of at least 79°. It shall be free from acidity, and shall not show more than traces of metallic salts or residual solvents. The average moisture of a lot shall not be greater than 0·1 p.c. The average ash of a lot shall not be greater than 0·1 p.c. It shall not contain more than 0·15 p.c. material insoluble in alcohol. It shall contain no free toluol, or impurity giving a nitric acid reaction with a sulphuric acid solution of diphenylamine. It shall contain not less than 18·20 p.c. nitrogen as determined by Dumas' combustion method. It shall give a heat test of at least 30 minutes at 65·5° with potassium iodide—starch paper.

Grade B. Crude.—The trinitrotoluene must be a high-grade material made from a suitable quality of raw materials. It shall be a yellowish, uniform, crystalline powder of such fineness that at least 90 p.c. will pass a sieve of 10 meshes per linear inch. It shall have a m.p. of at least 75·5°. It shall be free from acidity. It shall show not more than traces of metallic salts. The conditions as to ash, moisture, insoluble in alcohol, content of free toluol, and products giving a reaction with diphenylamine are the same as for the refined product. It shall contain not less than 18 p.c. nitrogen as determined by Dumas' combustion method.

One objection to the use of crude trotyl as a shell charge is that the lower melting impurities tend to exude as an oil during storage at a high temperature, and if this exuding oil penetrates to the priming or detonating charge this may be so deadened that failure to detonate results.

Liquid trinitrotoluene. The nitrated products recovered from the solvent used in the recrystallisation of crude trinitrotoluene, a thick brown syrup consisting essentially of a mixture of β and γ trinitrotoluenes, dinitrotoluene and a little mononitrotoluene is used in certain plastic explosive mixtures under the name of 'liquid trinitrotoluene.' A liquid product obtained by the direct nitration of crude trinitrotoluene is also used by this name, it is of similar composition except that it contains more α-trinitrotoluene and some un-nitrated hydrocarbons.

Properties.—Trinitrotoluene crystallises from alcohol in sulphur-yellow needles, but when petroleum or toluene is used the crystals are darker and of a light buff colour. Its colour is darkened by exposure to light; when freshly sublimed in the dark it is quite colourless. When pure, it is without odour and practically insoluble in cold water. It melts at 81·5°. It is soluble to a slight extent in hot water, and dissolves readily in alcohol, light petroleum, benzene, and other organic solvents. It dissolves in concentrated sulphuric acid at 90°–100°, and separates unchanged on cooling.

Crystals of trinitrotoluene have a density of 1·5, that of the solidified mass after fusion being 1·6.

Trinitrotoluene is chemically very stable, but undergoes very slight decomposition with evolution of gas at 180°. On application of a flame, trinitrotoluene burns with a hot but very smoky flame. It ignites more readily than picric acid, its ignition point being about 250°. It cannot be exploded by flame in the open and alone, and only quite locally by very strong percussion, but can be readily detonated by means of mercury fulminate. As much as 1000 kilos. have burned away quite quietly in a conflagration, and a rifle bullet may be fired through a solid mass without causing explosion; but disastrous explosions have occurred when very large quantities have been involved in a fire. It may be detonated in the powdered or finely crystalline form by means of a No. 3 detonator containing 0·54 gram fulminate composition, but when fused, it requires priming either with some of the loose powder, or other explosive such as 'tetryl.' Its velocity of detonation depends on its density, or degree of compression, but is about 7000 m. per sec. It is quite safe to handle, and is stable under very varying atmospheric conditions.

Trinitrotoluene is the most important of shell high explosives. Over picric acid it has the distinct advantages that it does not combine with metals, and, generally, has no acid properties. When pure its dust and vapour are not irritating or injurious to those working with it, and it has a considerably lower melting-point and is not so sensitive. It is slightly less powerful than picric acid in the ratio of about 91 : 100, and owing to its lower velocity of detonation has less shattering effect; but this is an advantage, since in the fragmentation of a shell the pieces are sufficiently large to have considerable destructive effect. The lower bursting effect of trinitrotoluene, as compared with picric acid, is attributed by Kast to its lower density and lower rate of detonation (6700 metres per second against 7100 metres per second). It is a less powerful explosive than wet guncotton, but its effect at a distance is greater, and it has replaced guncotton in most countries as a charge for torpedo war-heads and for submarine mines. It was first used in Germany in 1904.

Trinitrotoluene fulfils in a high degree the requirements of a military high explosive. The desirable properties are that it should be very powerful, but that its effects should not be too shattering or local, that it should be safe to handle, transport, and store under normal conditions of use, including those of a ship's magazine in a hot climate, that it should be chemically stable under all storage conditions, that it should be capable of certain and complete detonation, both in small and in large shell, under suitable impulse, but that it should be sufficiently insensitive to withstand the shock of discharge when fired in a big shell at full range.

Trinitrotoluene is deficient by 65·9 p.c. in oxygen for the complete combustion of its carbon and hydrogen, and by 22 p.c. when its carbon is burned to monoxide, and when detonated even completely free carbon is liberated in the form of thick black smoke.

According to Dautriche (Mem. Poud. et Saltp. 1911–1912, 27) when crystals are compressed into pellets at pressures varying from 275 to 4125 kilos. per sq. cm., trinitrotoluene has a density varying from 1·320 to 1·610, picric acid varying from 1·315 to 1·740, the velocity of detonation of the loose powder being 4100 metres per sec., picric acid being 5100, and of pellets at a density of 1·3 being 6200 m. per sec. for trinitrotoluene, and 6300 m. per sec. for picric acid. When 10 grams were fired in a standard lead block the expansion with trinitrotoluene was 216 c.c., that of picric acid being 228 c.c.

Shells are usually filled with trinitrotoluene, as with picric acid, by melting the compound and allowing it to solidify in the shells. Bichel (Fr. Pat. 357925, 1905) proposes to use compressed trinitrotoluene, which he had previously shown to have a higher velocity of detonation than in the loose condition, as an explosive for shells, mines, and torpedoes, by cementing together blocks of the compressed material by means of the fused compound, and, in a later patent (Fr. Pat. 369371, 1906), proposes to obtain a higher density than by simple casting, with trinitrotoluene as well as with other fusible nitro-explosives, by casting in a closed vessel, first placed under evacuation, to remove all air bubbles, and then submitting the molten mass, whilst rapidly cooled by means of a water-jacket, to compressed air or carbonic acid gas. A density as high as 1·69 has been obtained in this way.

Nobel (Ger. Pat. 212169, 1907), has patented a method of increasing the density of trinitrotoluene, and other suitable nitrohydrocarbons, by first cooling the shell to 0° before pouring in the liquid. Rudeloff, by compression under 3000 atmospheres, has obtained a mass with a density of 1·7, that can be cut and worked like wet guncotton. The detonation of the densified solid is facilitated by using some of the loose trinitrotoluene as a primer.

Trinitrotoluene is also used in considerable quantities for detonators. It is employed either alone, with a priming of mercury fulminate, or as an ingredient in cap and detonating compositions. It is, for example, stated that in a No. 7 detonator the 1·5 grams of fulminate can be advantageously replaced by a mixture of 0·7 gram of trinitrotoluene and 0·5 gram of fulminate.

Trinitrotoluene has been suggested in various mixtures as a high explosive for shells and torpedoes. Riehel (Fr. Pat. 369661, 1906) makes a plastic explosive called '*plastrotyl,*' by mixing it with a solid or liquid resin, such as copaiba balsam, or larch turpentine, with or without the addition of dinitrotoluene and collodion cotton. Rudeloff and Allendorff (Ger. Pat. 201306, 1906) make '*triplastit,*' with a density as high as 2·5 by mixing with a jelly prepared from dinitrotoluene and soluble dinitrocellulose, heating slowly to about 80°, and incorporating, as an oxygen carrier, a mixture of potassium chlorate and lead nitrate.

Trinitrotoluene is a constituent of many modern ammonium nitrate safety explosives, in which it has replaced the dinitrobenzene, which was more common in earlier mixtures, as it is not only more powerful but also less toxic.

Mixtures of ammonium nitrate with trinitrotoluene have been generally and largely used as a military high explosive for shells, bombs, grenades and mines. Sometimes a little wood meal and nitroglycerin are added to assist in the detonation, as in the German 'Astralite.'

Amatol. In this country the mixtures of ammonium nitrate and 'trotyl' are known as 'Amatol.' The mixtures are used in various proportions designated by a fraction of which the percentage of ammonium nitrate is the numerator, for example, 90/10, 80/20, 50/50, and 40/60. The proportions for complete combustion of the trinitrotoluene are 78·7 p.c. ammonium nitrate and 21·3 p.c. trotyl, so that 'Amatol 80/20' approximately fulfils this condition. Sometimes the mixtures are milled cold and 'stemmed' or rammed into the receptacles, sometimes, when the proportion of trotyl is high, this is melted and the plastic mixture is poured directly, or compressed into slabs and packed, into shells. These mixtures form powerful high explosives, somewhat more powerful than trotyl alone, owing to the more complete combustion, but the shattering effect is less than with trotyl alone, owing to the lower velocity of detonation which is of the order of 5000 to 6000 metres per sec., according to the proportions. The lower shattering effect is not necessarily a drawback. The mixtures are difficult to detonate, the difficulty increasing with the proportion of ammonium nitrate and with the degree of compression, and it is necessary to prime them with another explosive, when the use of a powerful fulminate detonator is inadmissible. They are hygroscopic, and precautions have to be taken to protect them from atmospheric moisture, and when efficiently detonated they are practically smokeless, giving only a slight grey or white cloud. Crude trinitrotoluene can be used for these mixtures, especially in those containing a large proportion of ammonium nitrate, as there is no danger of the impurities exuding as an oil on storage at high temperatures.

Other nitrohydrocarbons. Nitroxylenes. The mixed tri-, di- and mono- nitrohydrocarbons obtained by the nitration of the fraction of coal-tar distillate containing the three isomeric xylenes are used in some explosives. 'Monachit' is an ammonium nitrate explosive containing nitroxylenes, essentially the trinitro product. The nitrohydrocarbons, largely di- and trinitro derivatives of mesitylene and pseudocumene, obtained by nitrating solvent naphtha, have been proposed by Shulz and Gehre (Eng. Pat. 5687, 1905, and 19565, 1907) for use in explosive mixtures of the usual type, known as '*Vigorite*' and '*Bavarite.*'

The nitronaphthalenes, usually dinitronaphthalene, are occasionally used, principally associated with ammonium nitrate in safety explosive mixtures. Mononitronaphthalene occurs in the 'cheddites,' di- and tri- nitronaphthalenes in the 'Grisounit' and 'Ammonite' class of explosives.

The nitrohydrocarbons of the fatty series have so far met with only a limited use. The Soc. anonyme d'Explosifs et de Prod. Chim. (Fr. Pat. 394992, 1907) claim the use in particular of mononitromethane, a liquid boiling at about 99°-100°, in smokeless powders with nitrocellulose, or nitrocellulose and nitroglycerin, and the use of tetranitromethane by Winand has already been mentioned under 'Sprengel Explosives.'

Nitrophenols.

The potassium salt of mononitrophenol can be detonated by percussion, and it has been proposed in America (U.S. Pat. 792716, 1905, and 940580, 1909) to use dinitrophenol mixed with picric acid, to lower the melting-point of the latter, and as an ingredient in explosive mixtures, but the only nitro derivative of ordinary phenol used to any extent is picric acid, symmetrical trinitrophenol, which is largely used by itself as a high explosive, and to a limited extent in explosive mixtures, usually of the detonating class.

Dinitrophenol is used occasionally in mixtures of nitro bodies used as explosives, but is usually an intermediate product in the manufacture of picric acid from benzene. The benzene is first chlorinated, the chlorbenzene nitrated, and the resulting dinitrochlorbenzene heated with caustic alkali. The dinitrophenate is finally decomposed with hydrochloric acid, and the dinitrophenol washed and purified as usual. When pure it is a yellow crystalline substance, melting at 113·1°. Ellis and Wells (U.S. Pat. 1220078, 1917) nitrate the chlorbenzene by heating with sodium nitrate and sulphuric acid.

Picric acid. *Manufacture.*—Direct nitration of phenol with strong nitric acid gives picric acid, but the action is very violent, and there is considerable loss by oxidation, and it is preferable, therefore, to sulphonate the phenol before nitration. The reactions are:

(1) $C_6H_5OH+H_2SO_4=C_6H_4(SO_3H)OH+H_2O$

(2) $C_6H_4(SO_3H)OH+3HNO_3$
$=C_6H_2(NO_2)_3OH+H_2SO_4+2H_2O$

In the old method of manufacture of picric acid, which is still largely used, very simple apparatus is used, little or no care is taken in temperature control of the process, and considerable waste of sulphuric and nitric acids occurs, clouds of nitrous fumes from the nitrating pots being allowed to disperse over the surrounding country. A pure quality of phenol is taken, obtained either by careful fractionation of the coal-tar product or the synthetic material, and melted in its drums in a steam-heated chamber. The hot molten phenol is poured into about five times its weight of concentrated 98 p.c. sulphuric acid, from which the lead sulphate has been allowed to settle, contained in iron or enamelled-iron vessels, frequently ordinary household baths, arranged round a shed. The mixture is stirred occasionally with wooden or iron paddles for about two days, until the product is in the form of a solid white paste, without phenolic odour and completely soluble in water. A charge of the sulphonate and excess of sulphuric acid, sufficient to require a whole carboy of strong nitric acid for its nitration, is weighed out into the nitration pot, a little water is added and the mixture stirred occasionally during the day. The earthenware nitration pots, arranged in rows down a long shed open at the sides, are embedded in a non-conducting mass of ashes or similar material. A carboy of nitric acid is placed at the side of, and above the level of, the nitrating pot, and a narrow glass siphon arranged so that the nitric acid passes in a thin stream into the midst of the mixture during the night. The mixture is not stirred and the pots are unattended during this time. The mixture sets solid, but is stirred occasionally during the next day to complete the nitration, after the orange to red coloured crusts of low melting-point material have been removed, for sale as second-grade material after washing. The preliminary washing of the product is carried out in wooden boxes, with inclined bottoms perforated at the lower end, by pouring a few buckets of water over it. For the final washing the contents of several boxes are emptied into baths similar to those used in the sulphonation stage, water is run in from a tap and the contents of the bath stirred by hand with wooden paddles, the wash water, like that from the preliminary washing, being run away down a drain or gully to a small pond, by opening the plug of the bath. Three or four such washings are found to efficiently remove the mineral acidity. The completion of a batch of picric acid by this process takes about a week.

In more modern practice, the sulphonation is carried out in large iron lead-lined tanks or 'kettles,' fitted with a steam jacket and paddle agitators. As the mixture is kept hot and agitated a smaller proportion of sulphuric acid is required, 3½ to 4 parts being used. The nitration is sometimes carried out in earthenware pots, as above, but fitted with covers and fume pipes leading to a stack; but the most modern method is to have the nitration pots of enamelled iron and jacketed, and nitration is temperature controlled by the circulation of hot or cold water. The temperature of the hot sulphonate is allowed to fall to about 20°, and whilst rapidly agitated, the nitric acid is gradually run in, the quantity used being about four-thirds that theoretically required. The temperature is allowed to rise gradually during the addition to the nitric acid of about 70°–80°, and the nitration completed by further agitation for about 2 hours. The nitrous fumes evolved are condensed and reconverted into nitric acid. The product is run off into wooden or enamelled vessels, diluted with about an equal volume of water, and allowed to cool. The crystals of picric acid are filtered off, often with use of a vacuum, and washed by a spray of water in a centrifuge, until practically free from sulphuric acid. The crystals, owing to the agitation, are small and free from aggregations, are pure and readily washed.

A further quantity of picric acid is obtained in the early part of the concentration of the spent sulphuric acid. The final washing is sometimes done with alcohol: this gives a purer product as the alcohol dissolves resinous impurities, and also facilitates the drying of the picric acid, the alcohol being recovered.

Large quantities of picric acid are now produced, especially on the Continent, by the direct action of sulphuric acid and sodium nitrate on phenol; the difficulty in freeing the picric acid from sodium sulphate is one objection to this process.

Drying, grinding and sifting. The preliminary drying of the picric acid, sometimes filled into large canvas bags, is effected in the centrifugals. For the final drying, the picric acid is spread out, in stoves or sheds, on broad glass shelves, the glass being strengthened by wire-netting insertion. In some stoves the shelves are of enamelled iron or of aluminium, but wet picric acid has a slight action on aluminium. The stoves are heated by steam pipes below the shelves, and the acid is turned over occasionally with wooden rakes until dry. The dry acid is fed by means of a hopper through a sieve worked mechanically into a closed chamber, from which the material is packed. Lumps and aggregations of crystals left on the sieve are ground in an edge-runner mill and re-sieved. The drying and grinding of picric acid are dangerous operations, and whenever possible are not performed in the picric acid works, the product as it leaves the centrifugals being transported in the damp condition to the explosives factory. With this precaution and care to avoid contact between the damp picric acid and metals, except aluminium and tin, the manufacture of picric acid is practically free from danger.

To obtain more perfect purification from the last traces of mineral acids, picric acid may be converted into its sodium salt by dissolving in hot solution of sodium carbonate. On cooling, almost chemically pure sodium picrate crystallises out; this is centrifugated, washed with cold water, dissolved again in hot water, and the acid precipitated by adding an excess of hydrochloric acid. This is finally purified by washing and centrifugation, and the last traces of acid are volatilised on drying.

Gutensohn (Eng. Pat. 16628, 1900) proposes to add the phenol, dissolved in paraffin or similar oil, directly to the nitric acid, covered with a layer of the same oil, in order to moderate the nitration reaction without sulphonation.

Wenghöffer (Ger. Pat. 125096, 1900) suggests aniline as the primary material instead of phenol, as being less subject to variation in market price. It is converted, through sulphanilic acid, into diazobenzene sulphonic acid, which readily yields picric acid on nitration, a yield of 90 p.c. of the theoretical being claimed.

Hepp (Annalen, 1882, 344) suggested the preparation of picric acid from benzene by first converting this into trinitrobenzene, and then oxidising the product with a mild oxidising agent such as an alkaline solution of potassium ferricyanide. He claimed a good yield, and successful commercial manufacture based on this suggestion is said to have taken place, but the difficulty in the trinitration of benzene would seem to throw doubt on this.

Properties.—Picric acid crystallises in bright pale-yellow plates or prisms. When recently sublimed in the dark it is quite colourless, and the colourless tautomeride is also the stable form in contact with strong acids. It is sparingly soluble in cold, but more soluble in hot water. It has an exceedingly bitter taste, and its taste and colour are imparted to very dilute aqueous solutions. It is readily soluble in alcohol, acetone, ether, and benzene. It melts at 121·6° to a yellow liquid, and by careful heating may be sublimed without decomposition, the vapours being very bitter and irritating. Picric acid ignites at about 260°. Suddenly heated, it deflagrates sharply, with a bright-red sooty flame, and Berthelot has shown that a small quantity dropped on a red-hot surface decomposes with explosive violence.

Large masses of picric acid can be heated in a confined space without explosion, but Berthelot is of the opinion that the explosion of a small quantity by a heated surface may, under certain conditions, cause detonation of a large mass of picric acid. Some big explosions following fires at picric acid works are to be explained in this way.

It is difficult to explode picric acid by direct percussion, but it can be readily detonated by mercury fulminate; 1·5 grams of fulminate act well for the dry powder; even wet picric acid, containing as much as 15 p.c. of water, can be so detonated if a priming of the dry acid is used.

The heat of formation of picric acid is 49·1 cals., and the heat of total combustion in oxygen 618·4 cals. (Berthelot).

Picric acid does not contain sufficient oxygen for complete combustion, and it is 3·49 p.c. deficient for the formation of carbon monoxide, and 45·41 p.c. deficient for the formation of carbon dioxide. Nevertheless, when efficiently detonated, it is one of the most powerful explosives known, exceeding dynamite and compressed guncotton in power, especially when densified by fusion and solidification. Complete detonation is accompanied by a black smoke. The density after casting is 1·6–1·7, and it can be obtained with a still higher density by Bichel's method of casting under pressure.

Picric acid was first suggested for use as a semi-explosive ingredient in propellant explosives. Sprengel (Chem. Soc. Trans. 1873, 803) was the first to call attention to the explosive possibilities of picric acid in itself, but it was not till 1886 that Turpin made a practical high explosive of it, by suggesting the use of compressed or molten picric acid as a charge for shells. The value of picric acid as a high explosive lies in the fact, as Turpin pointed out, that in this class of explosives the maximum effect does not coincide with complete combustion, but occurs where the carbon is burnt to carbonic oxide, the greater gas evolution more than counterbalancing the smaller heat of combustion. Turpin's first '*Melinite*,' adopted in France as a high explosive for shells, was picric acid made into a colloidal state and densified by the addition of a solution of 3–5 p.c. collodion cotton in alcohol and ether, but very soon this was abandoned in favour of the fused picric acid alone, as Turpin showed this to be still more powerful, and so insensitive that it could only be detonated under strong confinement. Picric acid was adopted for use as a high explosive in Germany in 1888. The English '*Lyddite*' is simply fused picric acid, melted in large cans of copper tinned, of aluminium, or enamelled iron, in a carefully regulated hot-air stove, at 130°–140°, and filled directly into the shells, a central cavity being left for the exploder. Picric acid has been used for similar purposes, also for mines and torpedoes, by most other countries under various names, such as 'Ecrasite,' 'Shimose,' 'Pertite,' 'Picrinit,' &c.; in some cases additions of other substances, such as nitronaphthalene, di- and trinitrotoluene, trinitrocresol, being made in order to reduce the melting-point. As the melting-point of picric acid is so high, and its sensibility to percussion increases with the temperature, its fusion on the large scale is to some extent dangerous. Girard (Eng. Pat. 6045, 1905) gives a long list of the melting-points of equimolecular mixtures of picric acid with other nitro derivatives; in all cases the melting-point of the mixture is well below that of the constituent of lower melting-point.

The cast picric acid, when unconfined, is much more difficult of detonation by mercury fulminate than the loose acid; 3 grams of fulminate fired in the mass will not explode it. It may be detonated by using a priming of the loose acid or of guncotton, but much more perfectly by a primer of 'picric powder,' or trinitrotoluene.

On the assumption that the explosion of 'lyddite' is represented by the equation:

$$2C_6H_2(NO_2)_3OH = 3CO_2 + 8CO + C + 3H_2 + 3N_2$$

de la Roque (Rev. de Chim. Industrielle, 11, 5) has calculated the following constants:—

Heat evolved at constant pressure per kgm. . .	853·4 kgm.-cals.
Heat evolved at constant volume per kgm. . .	876·0 " "
'Potential' (*i.e.* maximum work by unit weight, assuming complete gasification and adiabatic expansion) . . .	272,280 kgm.-metres
Volume of gas from 1 kgm.	683,453 c.c. at N.P.T.
Temperature of explosion .	2832°.
Pressure developed by the explosion of 1 gram in unit volume . . .	8086 kgms. per sq. cm.

Actual analysis has shown that, when explosion takes place, the decomposition is more complicated than this, the products being: carbon monoxide, carbon dioxide, nitrogen, nitric oxide, water, hydrocyanic acid, and residual carbon.

Picric acid is safe to manufacture and transport. The advantages of cast picric acid as a high explosive are many, its physical and chemical stability are very great, and it can be kept for an indefinite period under varying atmospheric conditions; it is difficult to ignite, and it is very insensitive to percussion; is quite safe from the danger of being fired by the shock of the discharge of guns of large calibre, yet when perfectly detonated it is extremely powerful in its bursting effects. On the other hand, there are such disadvantages as its high melting-point, the objectionable nature of its vapours, which not only dye the hair, skin, and clothing of those working with it, but are also extremely irritating, if not harmful. It is difficult to detonate completely, and incomplete detonation yields very deleterious gases. The most serious objection of all, however, is its acidic character, which leads to the formation, in contact with metals and some of their compounds, of picrates, many of which are highly sensitive, the picrates of lead particularly so. Serious accidents have resulted in the use of picric acid, which have been attributed to the formation of these compounds, and for this reason the interiors of the shells are varnished, and lead compounds are carefully guarded against in the lutings used on the screw threads on the shell plugs, and in all paints and varnishes connected with picric acid shells. Trinitrotoluene is free from most of these objectionable features, and it has consequently more or less replaced picric acid in its many uses.

Emmensite (Eng. Pat. 370, 1888), the invention of Emmens of the United States, is produced as crystals, said to be different from picric acid, by the action of fuming nitric acid of sp.gr. 1·52 on picric acid. The explosive was favourably reported upon by the U.S. War Dept., and is said to be satisfactory, both as a propellant and as a high explosive.

Picrates. The picrates, formed by the action of the acid on the metals, their oxides, hydroxides, or carbonates, are well-defined, crystalline compounds, which are quite stable under ordinary conditions, but they are all more sensitive to heat, friction, and percussion than the acid itself, particularly when free from water of crystallisation. This is true, to some extent, even of the alkaline salts, whilst the picrates, normal and basic, of some of the heavy metals, especially lead, are extremely sensitive and violent. Anhydrous ferrous picrate is very sensitive. The order of sensitiveness to percussion of some of the picrates most likely to occur is: lead, iron, cobalt, nickel, barium, copper, manganese, zinc, calcium, and sodium. They detonate with violence, and their detonation is sufficient to prime an indefinite amount of picric acid, and even wet picric acid may be involved. Ammonium picrate is the most insensitive. It has been proposed as a substitute for picric acid for use in shells, as it has no tendency to form dangerous picrates. The temperatures of ignition of picrates are given by Silberrad and Phillips (Chem. Soc. Trans. 1908, 474), and their relative sensitiveness by Kast (Zeitsch. f. d. Ges. Scheiss- u. Strengstoffw. 1911, 7, &c.). A very serious explosion of picric acid, near Manchester, in 1887, was caused by melted picric acid flowing on to litharge, detonating with it, and thereby acting as a primer, causing the detonation of all the picric acid present. In connection with this explosion, Deering showed that very rough mixtures of picric acid with litharge, red lead, lead nitrate, strontium nitrate, lime, &c., detonated violently, and were sufficient to prime a large mass of picric acid. Mixtures of picric acid with certain peroxides will fire spontaneously.

Explosive mixtures containing picric acid and picrates. Many years before picric acid was used as a high explosive, attempts were made to use it and the picrates in explosive mixtures. It was recognised that picric acid is deficient in oxygen, and, consequently, picric acid and the picrates were proposed to be used mixed with various oxidising agents. However, the insensibility of picric acid is largely due to its deficiency in oxygen, and for this reason the mixtures with oxidising agents are all much more sensitive to heat, percussion, and friction than the acid itself. Mixtures containing picric acid, with either nitrates, chlorates, chromates, or permanganates, are extremely unstable, and liable to undergo spontaneous explosion, owing to the slow displacement of the highly oxidising acids by the picric acid, in the presence of even traces of moisture, and many serious accidents have been caused by such mixtures. Attempts have been made to increase the stability of picric acid mixtures by coating the particles of the acid with an insensitive and protective film; for instance, Roth (Eng. Pat. 173550, 1886) proposed a mixture of picric acid and ammonium nitrate with a fatty drying oil, and Turpin patented various mixtures of picric acid with gum, oils, fats, collodion jelly, &c.; but the picrates are far preferable to the free acid in explosive mixtures.

The picrates of ammonium, potassium, or sodium are those most frequently used in explosive mixtures. In 1869 Designolle made mixtures of potassium picrate and charcoal with nitre, in proportions varying according to their use, for small-arm and cannon powders, and mixtures of potassium picrate and nitre for filling torpedoes and shells. These mixtures were made in much the same way as ordinary gunpowder; they gave very good results, and were in use for some time in the French Navy. 60 grams of the propellant powders were said to give the same result as 350 grams of ordinary gunpowder, and the intensity of action of the disruptive powder was nearly 70 p.c. of that of dynamite No. 1. In the same year, Brugére and Abel, independently, recommended mixtures of ammonium picrate and nitre. Brugére's powder was composed of 54 p.c. of ammonium picrate and 46 p.c. of nitre. It was insensitive to friction or shock, slow burning, nearly smokeless, in small arms quite as powerful as gunpowder, and non-erosive. Abel's mixture, 3 parts of nitre and 2 parts of ammonium picrate, was at first proposed for use in shells, but afterwards adopted in the Service, under the name of *Picric powder*, as an exploder for priming lyddite shells. It is very stable, burns only locally with slight deflagration on application of flame, and requires strong confinement to develop its force, when it is very powerful. At one time it was manufactured and granulated like

Designolle's mixtures, but a mixture of 57 p.c. of nitre and 43 p.c. ammonium picrate, dry mixed, was subsequently adopted. It is easier and safer to make in this way, and the product is also more stable, for the wetting in the old method of manufacture caused the formation of a little hygroscopic ammonium nitrate by double decomposition. Its theoretical decomposition is:

$$5C_6H_2(NO_2)_3ONH_4+16KNO_3$$
$$=22CO_2+18N_2+15H_2O+8K_2CO_3$$

Ammonium picrate, and more rarely, potassium picrate, mixed with the nitrates of barium, potassium, and ammonium, and other ingredients combustible and explosive, have been the subject of innumerable patents for so-called smokeless and safety powders, usually in America, Austria, or France. Detonating mixtures containing picrates and chlorate of potash have been proposed, and picrate of lead has been suggested for the same purpose. The picrate mixtures generally, however, are shunned in this country, owing to their chemical instability and the extreme danger in their storage and use.

Trinitroanisol, the methyl ester of picric acid, $C_6H_2OCH_3(NO_2)_3$, has been used to some slight extent as a high explosive in bombs by the Germans. Its manufacture is not easy, as the nitrating acids tend to attack the side chain. A method of preparation stated to give a 85 p.c. yield is described by Broadbent and Sparre (8th Int. Cong. App. Chem. 1912). 30 parts of anisol are added drop by drop to a mixture of 130 parts of nitric acid of sp.gr. 1·52, and 220 parts of sulphuric acid of sp.gr. 1·84, cooled to −5°C., the temperature being kept below 0° during the addition. The temperature is then allowed to rise slowly to 65°–70°C., and kept at this temperature for 20 minutes. The acids and mixture are kept constantly agitated during the addition and nitration. After cooling, the crystals of trinitroanisol are separated and washed, first with a 2 p.c. solution of sodium carbonate, and finally with water. The product was in the form of lemon-yellow crystals, melting at 64°–65°. It is nearly insoluble in water, but readily soluble in alcohol, ether, and acetone; sp.gr. 1·408 at 20°C. It has the same percentage composition as trinitrocresol, and similar explosive properties, that is, it is less powerful and less easily detonated than picric acid, but it has an advantage over the latter in that it does not form sensitive metallic salts. It is, however, slowly hydrolysed in the presence of water to picric acid, and more rapidly in the presence of alkali.

Trinitrocresol is manufactured from metacresol similarly to picric acid, and has very similar chemical and physical properties. It melts at about 107°. It is acidic and forms explosive salts. It has explosive properties similar to picric acid, and has been used, when cast, as a high explosive for shells and torpedoes, alone and mixed with picric acid. It contains less oxygen than picric acid, is less powerful, and less readily detonated. It requires priming, and guncotton is generally used for this purpose. In France it is known as '*Cresylite.*' In Austria the name '*Ecrasite*' has been from time to time applied to high explosives of different composition used for charging shells, but apparently always containing trinitrocresol or its ammonium salt. Trinitrocresol has been used alone or mixed with picric acid, and the ammonium salt has been used alone or mixed with nitre. The ammonium salt is a yellow crystalline solid, melting at about 100°. It burns without explosion unless strongly confined, and is insensitive to friction and percussion. It is stemmed into shells with a wooden rod, or compressed into slabs. A guncotton primer is generally used to ensure complete detonation, but it can be exploded with a 2-gram fulminate detonator. A mixture of trinitrocresol and picric acid in molecular proportions, melted together and mixed with an oxidising salt, has been proposed by Girard (U.S. Pat. 895254, 1908). The trinitrocresylates are more sensitive to friction and percussion than the parent body, and generally have properties similar to those of the corresponding picrates, the lead salt and those of the heavy metals being the most sensitive.

The *higher nitrophenols* are all more or less explosive and yield explosive salts, but they have, as yet, met with no practical use.

NITRIC ESTERS.

On nitration, the organic alcohols and carbohydrates yield true nitric esters, or organic nitrates, which are explosive compounds. The internal structure and explosive characteristics of the nitric esters are different from those of the nitro derivatives, but, unfortunately, this difference has not been recognised in the technical nomenclature. The products of nitration of all organic substances, that are explosives, are all technically known as nitro explosives.

With reducing agents, the explosive compounds of this class yield more or less the primary substance of the nitration, and not amino compounds, as do the nitro derivatives, and by the prolonged action of caustic alkalis they give the primary substance and an alkaline nitrate, together with other products of secondary reactions. A simple test serves to distinguish the two classes of nitro compounds. When shaken with sulphuric acid, in a Lunge nitrometer, the nitric esters yield their nitrogen as nitric oxide; the true nitro derivatives do not do so.

The nitric esters, generally speaking, are more powerful explosives than the nitro derivatives, but are less stable, more especially in the presence of foreign substances, such as residual traces of the nitration acids.

Alcohol Nitrates.

The *Nitroglycols* have been repeatedly suggested as explosives, usually for admixture with nitroglycerin. Matthews, Strange, and Bliss (Eng. Pat. 12770, 1912) suggested the nitration of glycols having the hydroxyl groups attached to adjacent carbon atoms, or the corresponding oxides, and the preparation of explosives by admixture of the product with equal weights of nitroglycerin or nitrocellulose, and Hough (U.S. Pat. 1206223, 1916) claims, as a method of preparation of glycol dinitrate, the nitration of 1 part of glycol with 7 parts of an acid mixture containing not less than 93 p.c., nor more than 96 p.c., of total acids, ecial claim being made for a mixture con- ining 35 p.c. HNO_3, 59 p.c. H_2SO_4, and 6 p.c. $_2$O. Hibbert (U.S. Pat. 1216367, &c., 1917) oduces explosives by dissolving a carbohydrate a solvent-medium containing a 1·2 glycol, d nitrating the solution. Similar explosives e made with a mixture of 1·2 glycols with hylene-, propylene-, and butylene-glycols and lyglycols, and a carbohydrate. For example, parts of cane-sugar are dissolved in about parts of a mixture of ethylene- and propylene- ycols, solution is effected by heating to 80°– 0°, the mixture cooled, and added slowly to 0 parts of a nitrating mixture containing qual parts of 95 p.c. nitric acid and 'oleum' ontaining 6–10 p.c. SO_3, cooled to about 5°. After mixing, with constant agitation, the emperature is allowed to rise to about 15°, nd the nitration completed in about 20 minutes. After cooling, the nitrated product is separated and purified by washing with dilute sodium arbonate solution, and then with water. The product forms a pale-yellow oil, and is claimed o be relatively non-volatile and of low freezing-point.

Stettbacher (Zeitsch. Ges. Scheiss- u. Sprengtoffw. 1916, 11, &c.) describes the preparation and properties of the tetranitrate of pentarythritol $C(CH_2OH)_4$. The tetrahydric alcohol is prepared readily and cheaply by a method described by Tollens, and its tetranitrate is said to be particularly stable, and to combine the explosive properties of nitromannitol and nitroglycerin, whilst being free from their disadvantages. It is very powerful, and is claimed to possess in a high degree the power of initiating detonation in other explosives, though more sensitive than tetryl, and is suggested as suitable for use in primers, percussion caps, and detonators.

Nitroglycerins.

Mono-, di-, and tri-nitric esters of glycerin are possible. Liecke, in 1865, stated that he obtained mono- and di-nitroglycerin by nitrating glycerol at 0° in a mixture of 1 volume of nitric acid, sp.gr. 1·4, and 2 volumes of strong sulphuric acid; and later said that when nitric acid of 1·3 sp.gr. is used the mononitrate is obtained, whilst the dinitrate and trinitrate are respectively obtained by using an acid of 1·4 or 1·5 sp.gr.

Henriot claimed to prepare the mono-compound by nitrating glycerol with a dilute nitric acid containing 3 parts of water to 1 of strong acid; and Wohl (Ger. Pat. 58957, 1890) suggested the use of the mono- and di- compounds for reducing the freezing-point of nitroglycerin.

Mikolajczak did considerable work in 1904 on mono- and di-nitroglycerin (Zeitsch. Glückauf, 1904, 629); and Will made a full investigation of their preparation, properties, and uses in 1908 (Ber. 41, 1107), from which work the following short description is taken.

Dinitroglycerin. Will prepared dinitroglycerin by the following modification of Mikolajczak's method of preparation. 10 parts of glycerol are slowly stirred into 33 parts of nitric acid, sp.gr. 1·5, kept at a temperature of below 0°, and the mixture allowed to stand for several hours at 10°. The mixture is then poured into 10 parts of water and neutralised with powdered marble. On standing, the greater part of the dinitroglycerin separates as an oil, the remainder being extracted by ether.

Will's method of preparation is to slowly run 100 parts of glycerol, with constant agitation, into 500 parts of ice-cold mixed nitric and sulphuric acids, 3 parts H_2SO_4 to 1 part HNO_3, and 9 parts of water to 100 parts mixed acids. The mixture is then poured into 10 parts of water, and the dinitroglycerin allowed to separate. The acid solution is then neutralised, extracted with ether, the ether distilled off, the separated dinitroglycerin washed with a little water, and dried over sulphuric acid.

Dinitroglycerin can also be obtained by dissolving trinitroglycerin in strong sulphuric acid, diluting the solution with water and extracting with ether.

Dinitroglycerin is a colourless or light-yellow oil, which solidifies below −13°, and distils without appreciable decomposition at 146°; sp.gr. 1·47. It combines with water of crystallisation, and is hygroscopic. It is poisonous like trinitroglycerin. It is soluble to the extent of about 8 p.c. in water, and in all proportions in dilute nitric and sulphuric acids. It is also soluble in ether, alcohol, chloroform, acetone, carbon tetrachloride, and petroleum spirit. In strong sulphuric acid, like the trinitrate, it is denitrated, giving first mononitroglycerin, and eventually glycerol. When dry it dissolves and gelatinises nitrocellulose.

Will succeeded in separating dinitroglycerin into two isomerides by taking advantage of the property of one of them to form a crystalline hydrate. Both isomerides, when dry, have explosive properties resembling those of trinitroglycerin, but become non-explosive in moist air through absorption of water.

Mononitroglycerin was obtained by Will, by a process of crystallisation, from the oil extracted with ether from the neutralised and concentrated aqueous mother liquor obtained in the preparation of dinitroglycerin. He obtained two isomerides, both crystalline solids, melting at 54° and 58° respectively, and freely soluble in water.

Nitrodiglycerin. When glycerol is heated for 7–8 hours at 290°–295°, it is largely converted into diglycerin, with a little triglycerin and higher polyglycerins. The diglycerin can be separated by fractionation, and on nitration gives a product almost identical in properties with nitroglycerin. If a mixture of glycerol and a little diglycerin is nitrated, the resulting product, which contains di- and tetra-nitrodiglycerin, has all the properties of nitroglycerin, but remains fluid at −15° to −20° (Will, Zeitsch. angew. Chem. 1906, 889).

Nitroglycerin. Ordinary nitroglycerin is the trinitric ester of glycerol. It was discovered in 1847 by Sobrero. In a letter to Pelouze (Compt. rend. 24, 247), he states that when glycerol is poured, with stirring, into a mixture of 2 vols. of sulphuric acid of 66° Baumé, and 1 vol. of nitric acid of 43°, cooled by a freezing mixture, the glycerol dissolves therein without perceptible reaction, and that on pouring the mixture into water an oily substance, heavier than water, is precipitated.

Sobrero described some of the properties of nitroglycerin, but did not analyse it.

No practical application of importance of the properties of nitroglycerin was made until 1863, when its preparation on a large scale was commenced by Nobel, who started two nitroglycerin factories near Stockholm and near Lauenburg. It was first called 'pyroglycerin,' afterwards 'glonoine oil,' and still later 'Nobel's blasting oil.' Between 1863 and 1865 increasingly large quantities of nitroglycerin were made and exported; but serious accidents occurred about the year 1866 in different parts of the world whither the nitroglycerin had been exported, and were followed by legislation on the part of several governments, prohibitive of its use. This restrictive legislation was met by Nobel by the introduction of dynamite in 1866–67, the carriage and use of this preparation of nitroglycerin being comparatively safe. Mowbray, before this time, had manufactured large quantities of nitroglycerin in Massachusetts, and it had been transported for use in the mines in the frozen state.

Manufacture.—The following is a short account of the manufacturing processes in general use for the manufacture of nitroglycerin, with special reference to some improvements adopted at the Royal Gunpowder Factory, Waltham Abbey (*see* Nathan and Rintoul, J. Soc. Chem. Ind. 1908, 1903). The chemical basis of the processes is essentially that of Sobrero's method of preparation, but the modern manufacturing plant is of entirely different type from that in use in the earlier factories, and the output has enormously increased.

Prime materials.—The *glycerol* used in the manufacture of nitroglycerin is the purest distilled glycerol obtainable, and practically anhydrous. The presence of impurities in the glycerol leads to the formation, on nitration, of bodies, which render the product unstable and liable to spontaneous decomposition. Its sp.gr. must not be less than 1·26, and it must be free from acid, lime, chlorides, and arsenic. It should also be free from fatty acids; in the process of distillation of the glycerol, fatty acids of the same boiling-point are apt to come over, and when nitrated are difficult to remove from the nitroglycerin. The total residue, after careful evaporation of the glycerol, should be less than 0·25 p.c., of which not more than 0·10 p.c. should be inorganic. Even these tests are insufficient to ascertain the suitability of a glycerol for nitration, and the final verdict depends on a practical nitration test on the small scale; 10 grams of the glycerol are poured very slowly into a mixture of 27½ parts of nitric acid of 1·50 sp.gr., and 72½ parts of sulphuric acid of 1·84 sp.gr. kept quite cold during the addition. The nitroglycerin, after separation, and also the waste acids, are allowed to stand some time in long burettes and the separated nitroglycerin ultimately collected and measured. The yield should be at least 200 p.c. by weight of the glycerol, and, further, no flocculent matter should separate out during the nitration.

At the present time, the various supplies of glycerol at Waltham Abbey are carefully blended to ensure uniformity of manufacture, the blending being performed in large iron tanks holding 10 tons. The glycerol is rendered fluid by heating with steam coils, run into an elevator, a strong steel cylinder or egg-shaped vessel, and thence forced by compressed air into a tank in the charge house, which is placed above the nitrating house. The charge of glycerol was formerly weighed, but it is now usually measured in the tank by means of a gauge glass. The glycerol must not be too heated, or, because of its reduced specific gravity, the weight of the charge deduced from the volume in the tank will be incorrect; yet, on the other hand, it must be fluid enough to easily run into the nitrating apparatus.

Acids.—To procure a good yield of pure nitroglycerin, the nitric acid should be practically anhydrous. If the nitric acid be too weak, lower nitrates are formed, which dissolve in the acid mixture. To increase the strength of the nitric acid, and to keep this strength up by removing the water liberated in the nitration, it is necessary to mix the nitric acid with strong sulphuric acid. Nitroglycerin is soluble in either acid, but not in a mixture of the two. The strengths of the two acids and their relative proportions have varied from time to time. In all early large-scale manufacture, the mixed acid was similar in strength and proportions to that used by Sobrero, but the mixture is now usually made from acids of the following description.

The *nitric acid*, prepared by the ordinary methods from sodium nitrate and sulphuric acid, or recovered from waste acids by denitrating, must be at least of 1·5 sp.gr. at 15·5°, and must not contain more than a small quantity of nitrous acid; usually not more than 1·5 p.c. is allowed, but sometimes the limit is as low as 0·5 p.c. The nitric acid should be also free from sulphates and chlorine.

Mowbray introduced the method of freeing the nitric acid from nitrous acid by heating it and passing a current of air through it. At Waltham Abbey, the nitric acid is made by the Valentiner process, which gives a product very free from nitrous acid (*v.* NITRIC ACID).

The *sulphuric acid* must be the purest and most highly concentrated obtainable. It must have a sp.gr. of at least 1·842 at 15·5°, and must contain not less than 96 p.c. by weight of the monohydrate. It should be as free from iron and arsenic as possible, as these substances cause reduction of the nitroglycerin.

Mixed acids.—These acids are mixed in the proportion of 3 parts of nitric acid to 5 parts of sulphuric acid, and glycerol is usually used in the proportion of 1–8 parts of the acid mixture, but in some factories the proportion of acid mixture is as low as 7 or 7½ parts. In this acid mixture there is present nearly 6 p.c. of water over that giving acid monohydrate, and within the last few years it has become a common practice to add Nordhausen sulphuric acid in such quantity as to combine with nearly all this excess of water, an increased charge and yield and less waste acid resulting.

Nathan and others have patented (Eng. Pat. 6581, 1903) the nitration of glycerol with a mixture of Nordhausen sulphuric acid and nitric acid, with the object of obtaining a larger yield; but Guttmann (Chem. Zeit. 1905, 939) holds that, beyond a certain point, increase in the concentration of either acid does not improve the yield of nitroglycerin, and, further, is deleterious to the quality of the product.

The Nordhausen acid is stored in iron drums and, like the other acids, is first transferred to a steel acid elevator or 'egg,' as it is termed, and thence forced by compressed air into the mixing tank. The large cylindrical steel mixing tanks hold about 60 tons of mixed acid. Nitric acid is run into the tank through a pipe extending to the bottom of the tank, and then the sulphuric acid added through a pipe in the cover, and the two mixed by compressed air; the fumes evolved pass through a fume pipe into condensing towers. Two tanks are used at Waltham Abbey, so that the mixed acid can be allowed to stand some days before use, in order to allow lead sulphate and other impurities to settle out, and also so that it may be analysed, and any necessary adjustment of composition made. The mixed acid is run from the tanks as required into an elevator, and forced into a cylindrical steel vessel in the charge house to a fixed level determining the charge.

Nitration.—Mowbray carried out the nitration of glycerol in earthenware pots, using a large number of them and small charges. Each pot contained about 17 lbs. of mixed acids, into which 2 lbs. of glycerol was allowed to drop by means of a siphon; the operation of nitration taking place simultaneously in all the vessels. He introduced an important improvement on the old mechanical stirrers, by using compressed air for mixing the glycerol and acids. In later factories large lead vessels with conical covers were used for the nitration, and agitation was effected by the combined use of compressed air and a stirring paddle or helix; the water working the latter being also used for cooling the mixture by passing through lead coils. The glycerol was allowed to fall on a disc fixed to the shaft of the paddles above the level of the acids, from which it was thrown in fine drops on to the surface of the acids. A process of nitration evolving new principles was introduced at Vonges in 1872 by Boutmy and Faucher, and subsequently worked on a large scale at Pembrey in South Wales. They separately mixed the glycerol with part of the sulphuric acid, forming sulphoglyceric acid, and the nitric acid with the remainder of the sulphuric acid. Each of these operations involves the liberation of heat, so that, when these cooled mixtures were themselves mixed, less heat was developed in the actual process of nitration. However, the nitration process takes some 24 hours for completion, and the danger of leaving the nitroglycerin for so long a time in contact with the mixed acids more than counterbalances any advantage derived from the smaller development of heat. Serious explosions took place in various factories using this process, and it is no longer used.

In most modern factories the nitrating apparatus (there are usually two in the building) is a large lead cylindrical tank with a convex or inclined bottom, standing in a wooden vat. Inside the former are lead cooling worms, through which cold water circulates, as well as between the tank and its wooden case. This water is, in many factories, artificially cooled by a refrigerating plant to 10° or less. The agitation is now usually performed in this country with compressed air only, at a pressure of about 0 lbs. per square inch, which is forced through pipes which are led down to and round the bottom of the tank. The tank is closed with a dome-shaped cover of lead, provided with a number of glass inspection windows, through which the various pipes for air, water, and glycerol pass. A glass tube to allow the colour of the fumes to be seen, which is connected with a pipe to carry away the fumes, and thermometer, also pass through the cover. The mixed acids are run in, from the tank in the charge-house above, and cooled to a temperature of about 16°. The glycerol is then introduced in a spray at the bottom of the tank, compressed air and a simple injection apparatus being used to produce the spray, the contents being kept in a constant state of agitation and well cooled. The rate of flow of the glycerol is regulated so as to keep the temperature of the charge below 22°–25°. If red fumes are noticed at any time in the fume pipe, the inflow of glycerol is cut off, and additional air blown through till the fumes cease. If the evolution of red fumes cannot be stopped, or if the temperature should rise above 30°, and not fall with the full air current on, serious local decomposition is indicated and the charge is at once drowned.

Two pipes, provided with earthenware cocks, leave the nitrating tank at its lowest point, both of which can be opened, in case of danger, and the contents of the tank quickly discharged into the drowning tank—a large wooden tank filled with cold water situated immediately below the nitrating tank, the contents of which can be agitated by means of compressed air.

The whole process of nitration, including the subsequent cooling down, takes about one hour.

In the nitration of glycerol some sulphoglyceric acid is formed, the amount increasing with the quantity of sulphuric acid in the mixed acids. When the waste acids are allowed to stand, the nitric acid partly decomposes this sulphoglyceric acid, and nitroglycerin separates out.

Separation.—In early factories the separation of the nitroglycerin was effected by slowly running the nitrated charge into a large bulk of water containing in lead-lined vats, kept in a state of agitation. The bottom of the tank was inclined and led to a tap through which the nitroglycerin was drawn, after separation had taken place. This method of indirect separation involved the loss of all the waste acids, and is now replaced by the following method of direct separation.

When the nitrated charge has cooled down, one of the taps at the bottom of the nitrator is connected with a lead bend, the tap opened, and the whole of the contents run off into the separating tank placed just below the level of the nitrator. The separating tank is made of stout sheet lead, and has a pyramidal bottom leading by means of a glass inspection cylinder to a branched horizontal lead pipe with earthenware stop-cocks. The top has a cover with glass windows and fitted with a fume pipe. Air pipes are led into the separator through the cover, one round the bottom of the tank, the other ending in the glass inspection cylinder. On one side of the separator is a glass inspection window, and on another side an earthenware cock situated about 4 inches below the surface of the nitroglycerin after separation has taken place. The nitroglycerin sp.gr. 1·6, gradually separates and floats on the mixed acids, sp.gr. about 1·735. Two thermometers pass through the lid, one ending in the nitroglycerin, the other in the acids. The temperature is not allowed to rise above 17°; if it shows a tendency to rise, the air current is turned on. If the temperature cannot be reduced, and red fumes are given off, the charge is led through a third cock at the bottom of the separator into the drowning tank. After the separation is complete, usually in about 40–45 minutes, the bulk of the nitroglycerin is run through the side tap into the 'preliminary washing tank.'

The waste acids are then run away through the bottom pipe to the 'after separating house.' When the nitroglycerin level is seen through the inspection cylinder, it is led through the second branch of the pipe into the pre-washing tank.

Any fatty acid impurities in the glycerol separate out as a vesicular scum, also containing silica, iron, and lead compounds, between the nitroglycerin and acid layers. Certain chemical and mechanical impurities also form a scum on the surface of the nitroglycerin. Any thick sludge collecting in the separator is led off through a fourth cock into the wash-water settling house.

Several suggestions have been patented to accelerate the separation. Möller, for the Dynamit Actien Gesellschaft of Hamburg (Eng. Pat. 13562, 1904), claims for the addition of a small quantity, 0·52 part per 100 glycerol, of fatty hydrocarbon or acid, or, preferably, high boiling paraffins, to the acids before nitration. Reese (Eng. Pat. 20310, 1905) attributes the slow separation to the presence of small quantities of colloidal silica and adds sodium fluoride to the nitrating acids, 0·002 part per 100 glycerol; on the other hand, the Westfalisch-Anhaltische Sprengstoff A. G. (Ger. Pat. 249573, 1911) add a silicate, such as kaolin or steatite, to assist separation, and the Rheinische Dynamitfabrik Ger. Pat. 283330, 1912) use both silica, kieselguhr, and hydrofluoric acid, or sodium silicofluoride, so as to produce silicon tetrafluoride. Haddan (Eng. Pat. 18597, 1907) claims that the nitroglycerin is rapidly separated from the nitrating acids by passing an electric current through the mixture between platinum electrodes, the gas bubbles formed during the electrolysis carrying the suspended nitroglycerin to the surface.

Nitration-separation.—In 1901 Nathan, Thomson, and Rintoul (Eng. Pat. 15983) patented an improved apparatus for the manufacture of nitroglycerin, which has been since used at the Royal Gunpowder Factory. The two operations of nitration and separation are carried out in one apparatus, and all earthenware cocks, which were a constant source of danger, are done away with, the separated nitroglycerin being displaced from the top of the apparatus by introducing waste acid below its level.

The nitrator-separator (J. Soc. Chem. Ind. 1902, 927) is a cylindrical lead vessel, with a bottom sloping in one direction, with the usual cooling coils and air pipes led in through the side just below the surface of the acid mixture. The cover, which is conical, and burnt on to the body, terminates in a small cylinder, provided with an inspection window, opening at the top into a fume pipe and also laterally into a gutter leading to the pre-wash tank. A thermometer passes through the cover. At the bottom of the tank is a pipe with three branches—one branch leads downwards to the drowning tank, another leads upwards and has two branches leading to the mixed acid and waste acid tanks respectively, the third leads to the denitrating plant.

The process is carried out as follows: After the nitrating acid is run in, and brought to the proper temperature, the glycerol injector is introduced and the nitration effected as usual In Continental practice an injector is never used, the glycerol being introduced through a bunch of 16 or 18 small tubes. The nitric acid fumes are condensed in a Guttmann's condensing tower, about 18 lbs. of nitric acid, of sp.gr. 1·320, being recovered per ton of nitroglycerin. After the nitration is completed, the mixture is allowed to stand for a few minutes, and then waste acid is gradually run in to displace the nitroglycerin as it separates. When the separation is complete, a clear line of demarcation between the nitroglycerin and the waste acid is seen in the inspection cylinder.

The apparatus is left full until required for another nitration. In this way the life of the apparatus is largely increased, as no part of the interior is left exposed to acid fumes. Removing the nitroglycerin from contact with the acid as it separates, and the cooling during separation, increase the safety of the manufacture.

Preliminary washing.—The nitroglycerin coming from the separator is run into circular lead-lined tubs filled with water. The bottom of the tank is inclined towards a cock, and there is another cock in the side of the tank above the level of the separated nitroglycerin, for drawing off the washing waters to the 'wash-water settling house.' Compressed air is blown into the tank whilst the nitroglycerin is running in in a thin stream. A thermometer is supported in the tank and the temperature is kept below 18°. After washing for a few minutes, the nitroglycerin is allowed to separate, and the wash water is run off. More water is run in and the process repeated, any further nitroglycerin from the separator being added. The washing process is performed four times, dilute sodium carbonate solution being added in the last washing, and the temperature raised to 15°. When the preliminary washing is completed, the nitroglycerin is run down a lead-lined gutter to the 'wash house.'

The pre-wash tank now in use at Waltham Abbey has a fixed cover with a fume pipe, and has no cocks. The wash water is run off by gradually depressing a rubber funnel, connected with the outlet, into the water, and the compressed air pipe is burnt to the under side of the tank, the air holes being pierced through the bottom. This does away with any possibility of friction, and the bottom of the tank is left smooth and is readily cleaned. The washed nitroglycerin is led off through a rubber tube leading on to a gutter, which carries it to the wash house. Compressed air is blown through this rubber tube into the tank during the washing, to keep it free from unwashed nitroglycerin.

Final washing.—The final purification of the nitroglycerin to remove the last traces of acid and other impurities is effected in a lead-lined tank, over which the gutter from the pre-wash tank projects. The tank has an inclined bottom leading to the nitroglycerin draw-off cock, and is fitted with compressed air pipes for agitating the contents. The wash waters, as they separate, are run off through a pipe near the bottom, connected inside the tank by a length of indiarubber tubing with the 'skimmer,' and indiarubber-covered metal funnel that can be gradually depressed below the surface of the liquid. Cold water from the main, or warm water from an adjacent tank, can be run into the tank through indiarubber tubes. The washing tank is fixed above a large drowning tank filled with water.

The nitroglycerin is first washed with dilute soda solution, about 2½ p.c. strength at a temperature of about 30°, hot or cold water being run in as necessary. Second, and sometimes third, washings are performed with weaker soda solution, and then lastly two washings with water only, still at the same temperature. The final washing leaves not more than 0·01 p.c. of alkali in the nitroglycerin.

The wash tank now used at Waltham Abbey is made of heavy lead without casing. The air pipe is soldered beneath the tank, there are no cocks, the skimmer is made entirely of rubber, and the nitroglycerin is run off through an indiarubber tube as from the pre-wash tank. The washing water is softened and filtered, and, like the soda solution, is stored in tanks in the charge house.

Filtration.—After the washing is complete, the nitroglycerin is usually filtered to remove moisture and suspended flocculent impurities, the operation being carried out in the washing house. The usual method is to filter through a flannel bag filled with salt, placed over a cylinder with a wire gauze bottom, into a lead-lined tank, with an inclined bottom. Sometimes two filters, one above the other, are used. The pure nitroglycerin is drawn off as required through a cock.

The present method at Waltham Abbey is to use a lead tank with a perforated false bottom, on which is placed a layer of dry sponges sewn up in flannel, and the cock is dispensed with, the rubber tube previously described being used. A sponge filter was used in the Boutmy-Faucher process.

In some factories filtering is not resorted to, but the water is removed by allowing the washed nitroglycerin to stand for some days in a warm room, when all the water rises to the surface of the nitroglycerin.

Testing.—The finished nitroglycerin is tested for moisture, alkalinity, and nitrogen content, and has to pass a specified time limit in the Abel heat test. (For a description of this test, *see* under stability tests, p. 92.)

Treating the wash waters.—All the wash waters, from washing the nitroglycerin or apparatus, which contain considerable quantities of nitroglycerin, are run down lead gutters into a large wooden tank in the wash-water settling house. The contents are kept in agitation during the day, and allowed to settle overnight. The separated nitroglycerin is run off in the morning, in the old form of tanks through a cock, in the new through an indiarubber tube, into indiarubber buckets and returned to the preliminary washing tank. The wash water is drawn off from above the level of the nitroglycerin and run into a 'labyrinth' or nitroglycerin trap, a long oblong lead tank divided into a series of compartments by partitions, with rows of holes, alternately at the top or bottom, for the water to pass through. Each partition has also one hole at the bottom, through which the deposited nitroglycerin runs and collects at the lowest point of the bottom, and is drawn off and treated like that from the wash-water settling tank. The water from the labyrinth is run into ponds, and any nitroglycerin collecting there is occasionally destroyed by detonation.

At Waltham Abbey, labyrinths are now also placed in the nitrating and wash houses, through which the wash water passes before going to the wash-water settling tank. By this means the nitroglycerin reaching the latter is materially reduced.

Secondary or *after-separation* from the waste acids.—The waste acids from the separator contain a small quantity of nitroglycerin, and a further quantity is formed on standing, as already explained, from the sulphoglyceric acid. The waste acids are run into large cylindrical lead vessels, surrounded by a water jacket and fitted with cooling worms and compressed air pipes. The top of the tank is closed by a conical lid with a glass cylinder at the apex; the acids being filled in to about half-way up this tube. The cover has also a fume pipe and two thermometers, one in the nitroglycerin, the other reaching to the acid. As the nitroglycerin separates, it is removed and poured into a small lead tank containing water, which acts as a prewash tank.

The cooling jacket, worms, and air current are only used if the temperature rises considerably during the separation. When no more nitroglycerin separates on standing (sometimes a week is necessary), the acids are run off and treated by some denitration process, and after concentration are again used in the manufacture.

The process of separation is no longer carried out at Waltham Abbey, but the waste acids are treated by a process patented by Nathan, Thomson, and Rintoul (Eng. Pat. 3020, 1903). The patentees take advantage of the facts that the addition of a small quantity of water to the waste acids not only absorbs the suspended finely-divided nitroglycerin, but also prevents the formation of more nitroglycerin on standing. The waste acids, after standing and cooling in the nitrator-separator and removing any additional nitroglycerin that separates (this separation is much more complete than ordinarily), the quantity of acid necessary for displacing the next charge is run off into an acid elevator and forced up into the displacing tank. The remainder of the waste acids is then violently agitated, but not cooled, and 2 p.c. of water is gradually added; the acid is then run off and forced into the tank in the denitrating house. On the Continent water is not added to the waste acids, but the after-separators are still retained, as they yield 0·8–0·9 p.c. nitroglycerin, calculated on the glycerin used.

Instead of the usual denitrating, Nobel (Fr. Pat. 351454, 1905) proposes to regenerate the waste acids by the addition of fresh acids, and claims in this way to increase the yield of nitroglycerin, and states that the process of nitration is rendered less dangerous.

Yield.—From the equation representing the formation of nitroglycerin:

$$C_3H_5(OH)_3+3HNO_3=C_3H_5(NO_3)_3+3H_2O$$

a theoretical yield of 247 parts of nitroglycerin should be obtained per 100 parts of glycerol. Up till recently a yield of 215 p.c. was considered very good, but now yields of 229 p.c. and over are usually obtained.

A charge of 1320 lbs. of glycerol has been used at Waltham for some years. Guttmann states that it is customary in well-conducted factories to nitrate 110 kgs. of glycerol, in a mixture of 300 kgs. of nitric acid of about 93–94 p.c. monohydrate and 500 kgs. of sulphuric of 96 p.c. monohydrate. This corresponds to about 255 parts of nitric acid monohydrate, and 436·4 parts of sulphuric acid monohydrate, or a total of 691·4 parts of acid monohydrate with 35·8 parts of water, 4·9 p.c. to each 100 parts of glycerol. He also states that the largest apparatus made in lead nitrates 680 kgs. of glycerol at one operation, whilst in America and South Africa steel apparatus with mechanical stirring gear are mostly used, some nitrating 1000 kgs. at a time. Factories using the nitrator-separator process now employ a mixture of 41 p.c. of nitric acid, 57·5 p.c. sulphuric acid, and 1·5 p.c. water, corresponding to 250 lbs. nitric acid, 350 sulphuric acid, and 9 lbs. of water for each 100 lbs. of glycerol, which gives a ratio of 6·09 of acid to 1 of glycerin. The Thomson apparatus is now generally used on the Continent with slight modification in the procedure. The nitration is carried out at a temperature of from 28° to 30°, by 6 parts of an acid mixture containing 44 p.c. HNO_3, 55 p.c. H_2SO_4, and 1 p.c. H_2O. This more drastic nitration is stated to give a purer product by oxidation of some of the impurities usually found, with a yield of from 232 to 233 p.c. Hofwimmer (Chem. Zeit. 1912, 961) states that a maximum yield of nitroglycerin is obtained by the use of 3 molecular weights of sulphuric acid and 4 of nitric acid for the nitration of 1 molecular weight of glycerin.

Composition.—By sufficient dilution with copper oxide, the combustion of nitroglycerin can be carried out in the ordinary way. The nitrogen can be estimated by Dumas' method, or, better, by the nitrometer. The results of numerous analyses by different experimenters give figures very closely corresponding to the theoretical composition $C_3H_5(NO_3)_3$; and Perkin (Chem. Soc. Trans. 1889, 726) from determinations of the magnetic rotation of nitroglycerin, concludes that nitroglycerin must have its oxygen combined in the form $-O-NO_2$.

Properties.—Nitroglycerin is a heavy oily liquid; its sp.gr. at 15·6° is 1·60. When properly made from perfectly pure and colourless glycerol and acids, it is as colourless as water; but of a yellow to pale-brown colour as obtained on the commercial scale, according to the purity of the prime materials. It is neutral in reaction, and, when quite free from water, it is transparent. When pure, nitroglycerin may be kept for an indefinitely long time without decomposition. Thus Berthelot records the keeping of a specimen for 10 years, McRoberts one for 9 years, without any appearance of decomposition. But the presence of moisture, or of a trace of free acid, is able to start the decomposition of nitroglycerin; sunlight also causes it to decompose (Berthelot).

A mixture of ozone and oxygen, according to Beckerhinn, oxidises nitroglycerin at ordinary temperatures, with the formation of glyceric and nitric acids. When nitroglycerin does decompose at ordinary temperatures, the decomposition proceeds quietly, the liquid turns green, and NO_2 and CO_2 are evolved. After some time, the whole mass gelatinises, and contains much oxalic acid and ammonium salts. Nitroglycerin solidifies into long white prismatic needles, the temperature at which it solidifies varying with different samples between +8° and -11°; the frozen nitroglycerin melts again at about 11°. The time of exposure for solidifying or melting must be prolonged. Nauckhoff found that pure nitroglycerin could be cooled to as low a temperature as -40° to 50° without solidifying, though he states its true freezing-point to be 12·3°. When cooled by a mixture of solid carbon dioxide and ether, it solidifies to a glassy mass. Kast (Zeitsch. f. d. Ges. Scheiss u. Sprengstoffwesen, 1906, 225) has shown that nitroglycerin exists in two allotropic forms, one solidifying at 13·2°, the other at 2·1°, the melting-points being 13·5° and 2·5° respectively. Will (Ber. 1908, 1107) gives the melting-point of the labile modification as 2·2°, and of the stable modification as 12·2°. Hibbert (8th Int. Cong. App. Chem. 1912) describes the preparation of the two solid forms of nitroglycerin and states that the labile form crystallises in the triclinic system, and has a m.p. of 2·0°, and a freezing-point of 1·9°; whilst the stable form crystallises in the rhombic system, and has a m.p. of 13·2°, and a freezing-point of 13·0°. The labile form is comparatively stable below 0°, but is converted at once to the stable form with rise of temperature on addition of a crystal of the latter.

Nitroglycerin is slightly volatile at ordinary temperatures, the volatility increasing with rise of temperature. Marshall and Pease (Chem. Soc. Trans. 1916, 109, &c.) have determined the vapour pressure of nitroglycerin, by the amount volatilised from cordite at various temperatures. They obtained the following results: at 20°, 0·00026 mm.; at 30°, 0·00083 mm.; at 40°, 0·0025 mm.; at 50°, 0·0072 mm.; at 70°, 0·044 mm.; and at 80°, 0·098 mm. According to Hess, it can be completely evaporated by continuous exposure to a temperature of 70°, and it can be distilled *in vacuó* below 100°. Will states that nitroglycerin can be completely volatilised at 160° without boiling. Champion gives the boiling-point as about 185°, but de Bryn states that this temperature is too low, and that the boiling-point is over 200°.

Although perfectly pure nitroglycerin is quite stable at ordinary temperatures, it soon begins to decompose at slightly elevated temperatures, the decomposition rapidly accelerating owing to the catalytic action of the decomposition products, so that it soon becomes dangerous. According to Guttmann, a temperature of between 45° and 50° is the critical one for nitroglycerin, the stability being practically perfect below this temperature. The decomposition is accelerated by small traces of nitrous acid; by the oxidation glyceric and oxalic acids are formed.

The velocity of decomposition of nitroglycerin, when out of contact with the products of decomposition, has been examined by Robertson (Chem. Soc. Trans. 1909, 1241). He concludes that the nitrogen is disengaged almost entirely as nitrogen peroxide, in which respect the decomposition differs from that of guncotton; that the disengagement of nitrogen peroxide proceeds in a perfectly uniform manner; that the rate of decomposition is a function of the temperature, and increases from 95° to 125°, being doubled in a rise of 5°, and that nitroglycerin has a higher rate of decomposition than guncotton under similar conditions.

Mowbray found that his nitroglycerin contracted about $\frac{1}{12}$ of its original volume on freezing.

Beckerhinn made a number of estimations of the specific gravity of Nobel's nitroglycerin, which was procured from different factories. The specific gravity of the solid nitroglycerin was taken at +10° (nearly at its melting-point); all the nitroglycerins gave very concordant values, having a specific gravity of 1·735. The specific gravity of the liquid nitroglycerin was found by numerous estimations to be 1·599; whence, in solidifying, nitroglycerin contracts about $\frac{10}{121}$ of its original volume. Consequently, Nobel's and Mowbray's nitroglycerin agree in this respect.

Beckerhinn found for the specific heat of liquid nitroglycerin (between 9·5° and 98°) the value 0·4248, and for the latent heat of fusion of solid nitroglycerin the value 33·54 heat-units.

Perkin (*l.c.*) found the magnetic rotation of nitroglycerin to be 5407.

It is inodorous, has a sweet, pungent, aromatic flavour, and even in very small quantity has toxic properties, first noticed by Sobrero. Schuchardt (Dingl. poly. J. 180, 406) tried the effect on himself of swallowing a drop of nitroglycerin. He soon experienced vertigo, headache, lassitude, and drowsiness; and an hour later, having incautiously taken more nitroglycerin, the symptoms mentioned increased in severity, and were followed by nausea and loss of consciousness. No ill effects were, however, felt next day.

The handling of nitroglycerin is followed by similar unpleasant symptoms; but continued handling of the nitroglycerin for a day or two gives immunity from the headache. The chief symptom is usually violent headache. Fresh air, drinking black coffee, or extract of sarsaparilla, and the administration of morphine acetate, are antidotes.

Hay states that 1 gram of nitroglycerin dissolves in about 800 c.c. of water, and in 4 c.c. absolute alcohol. Will gives the solubility in water at 15° as 0·16 p.c., and the absorption of water as 0·2 p.c. It is freely soluble in methyl alcohol, ether, benzene, nitrobenzene, chloroform, acetone, glacial acetic acid, ethyl acetate, and other organic solvents.

It is practically insoluble in glycerol and in carbon disulphide. The solubility of nitroglycerin in a large number of solvents is given by Elliott, in the School of Mines Quarterly, iv. 15. Nitroglycerin is soluble in strong nitric acid, unchanged; in strong sulphuric acid it is dissolved and gradually denitrated with the formation of glyceric sulphate.

Berthelot (Sur la Force des Matières explosifs d'après la Thermochimie, 1883) gives for the heat of formation of liquid nitroglycerin from liquid glycerol and nitric acid, +14·7 kgm.-degrees per molecule (227 grams) of nitroglycerin; and for the heat of formation of nitroglycerin from its elements (diamond carbon, gaseous hydrogen, nitrogen, and oxygen), +98 kgm.-degrees per 227 grams; or, +432 gram-degrees per 1 gram nitroglycerin.

Detection.—Nitroglycerin can be detected by its taste, and by absorbing a drop on bibulous paper; the drop produces a permanent greasy stain which explodes when struck by a hammer on an anvil, burns with a yellowish-green flame, with a cracking sound, or, when heated from below, explodes with a loud report. It is soluble in methyl alcohol, the solution becoming milky on the addition of water, and eventually depositing heavy oily drops. A solution of 1 vol. of aniline in 40 vols. of sulphuric acid, sp.gr. 1·84, gives a purple-red colouration with the smallest trace of nitroglycerin (Werber).

Reactions.—Of the reactions of nitroglycerin two may be mentioned. The decomposition of nitroglycerin by caustic potash was stated by Railton (Chem. Soc. Trans. 1855, 7, 222–224), to be:

$$C_3H_5(NO_3)_3+3KOH=C_3H_8O_3+3KNO_3$$

but this was not at all justified by the results of his experiments, as only a small fraction of the nitroglycerin seems to have been decomposed, and the formation of some potassium nitrate and glycerol to have been only qualitatively determined.

Hay (*l.c.*) states that, by the action of alkalis on nitroglycerin, glycerol is not regenerated, but is oxidised at the moment of formation at the expense of the nitric acid, potassium nitrite being formed. He sums the reactions into one equation, thus:

$$C_3H_5(ONO_2)_3+5KOH$$
$$=KNO_3+2KNO_2+HCO_2K+CH_3CO_2K+3H_2O$$

stating that while the oxidation products of glycerol may vary as regards their nature and proportions, the above equation expresses with approximate accuracy the course of the reaction. Berthelot (Compt. rend. 1900, 131, 519) considers that the regeneration of potassium nitrate may be taken as corresponding to that of the glycerol, and, if that is so, the production of potassium nitrite implies the simultaneous formation of a more highly oxidised product, such as glyceric aldehyde, in this way:

$$C_3H_5(NO_3)_3+3KOH$$
$$=C_3H_6O_3+H_2O+2KNO_3+KNO_2$$

Berthelot also considers that the poor stability of some samples of nitroglycerin, for which it is often difficult to account, may be attributed to the formation of glyceric aldehyde in the manufacture, produced in this way:

$$C_3H_8O_3+HNO_3=C_3H_6O_3+HNO_2+H_2O$$

and that this nitrous acid may then form a mixed ester of the composition $C_3H_5(NO_3)_2NO_2$; both of which impurities would be difficult to detect.

In work on the hydrolysis of nitro-glycerin in alkaline solution, Silberrad and Farmer (Chem. Soc. Trans. 1906, 1759) attribute the absence of glycerol in the products to its degradation to hydroxy-acids, &c., owing to the more reactive condition of the nitric acid when first set free on hydrolysis. Nitroglycerin is acted on by potassium hydroxide in aqueous and in alcoholic solution; but, naturally, much more slowly by aqueous potash.

The reaction of nitroglycerin with alkaline sulphides, by which glycerol is formed with reduction of the NO_2 group, and not an amido derivative, is of great theoretical interest, but has not been examined quantitatively as in the case of guncotton.

Some experiments were made in 1883 by Bloxam (Chem. News, 47, 169), on the decomposition of nitroglycerin by alkaline sulphides, but more with the view of finding a safe means of disposing of nitroglycerin. He found that alcoholic solution of KHS, strong aqueous solution of K_2S, aqueous yellow ammonium sulphide, the orange-coloured solution of calcium sulphide formed by boiling flowers of sulphur and slaked lime with water, are all able (the last solution more slowly than the others) to effect the conversion of nitroglycerin into glycerol.

Combustion and detonation.—Heated rapidly to 200°, nitroglycerin inflames, and at a little higher temperature detonates with great violence (Berthelot, Sur la Force des Matières explosifs).

The temperature of explosion of nitroglycerin is variously stated. Nobel states that when heated to 180°, it explodes. Hagen gives 180°–190° as the temperature of explosion of nitroglycerin; Leygue and Champion give a higher temperature. F. Hess observes that explosive substances, when slowly heated, detonate at a lower temperature than when suddenly heated. The temperature of explosion of nitroglycerin (and of explosives in general) is evidently dependent on the conditions of the experiment. McRoberts (*l.c.*) says that the explosion of nitroglycerin can be brought about by heating it to a temperature at which decomposition takes place; the decomposition itself then speedily raises the temperature to the point of explosion. Snelling and Stone (U.S. Bureau of Mines, Tech. Paper No. 12) have studied the behaviour of nitroglycerin on heating. The nitroglycerin gradually became yellow, then orange, as the temperature was raised, obvious decomposition with gas evolution and partial distillation took place at 145°, and explosion occurred at about 218°. They explain that the lower explosion temperatures given by other observers are due to the heat of decomposition of the nitroglycerin locally raising the temperature above the recorded temperature of explosion.

Nitroglycerin is not readily inflamed at atmospheric temperatures by contact with flame or with a red-hot body. Thus, Nobel in 1865 showed that nitroglycerin was not inflamed when its surface was touched with a red-hot iron rod; the flame of a burning wood-shaving set on fire nitroglycerin, which burnt without explosion with a flame that went out when the source of heat was removed; and he states that burning nitroglycerin explodes only when its temperature is raised by the combustion to at least 180°.

Electric sparks will inflame nitroglycerin, but with difficulty. Abel placed two poles connected with a Ruhmkorff's coil, in some nitroglycerin and passed sparks between them; the surface of the nitroglycerin was agitated, turned black, and after half a minute the nitroglycerin exploded.

The combustion of nitroglycerin, brought about by contact with an ignited body, gives rise to nitrous vapours and a complicated reaction; it burns with a yellow flame, but without explosion properly so called, at least in the case of small quantities. But if the quantity of nitroglycerin is too large, the combustion ends in detonation. The gases produced by burning nitroglycerin (or, rather, ordinary dynamite: nitroglycerin and silicious matter) have been analysed by Sarrau and Vieille. The gases were allowed to escape freely, under approximately atmospheric pressure; they had the following composition per 100 volumes of gas:—

NO	48·2	H	1·6
CO	35·9	N	1·3
CO_2	12·7	CH_4	0·3

The combustion, therefore, under these circumstances appears to be very incomplete.

In the early days of the use of nitroglycerin, Nobel effected its explosion in a borehole by means of the explosion of gunpowder (Nobel, Eng. Pat. 2359, 1863). The gunpowder was fired by a fuse, but the explosion of the nitroglycerin was uncertain and incomplete. Incomplete detonation of nitroglycerin leads to its combustion and the formation of nitric oxide and the deleterious higher oxides on coming in contact with the air. Subsequently (in 1864) Nobel exploded the nitroglycerin by means of the detonation of mercury fulminate contained in a strong copper cap, or detonator, as it is now termed, immersed in the liquid. The detonation was then complete, and the force developed much greater than when the nitroglycerin was fired by means of gunpowder.

The shock of two hard bodies capable of vibrating readily is able to cause the detonation of nitroglycerin coating the struck surfaces. Nobel noticed that a film of nitroglycerin on an anvil, struck lightly by a hammer, detonated only where struck by the hammer; but if struck heavily, the whole film of nitroglycerin detonated (McRoberts, *l.c.*). If the film be covered only with a sheet of paper, and struck, the detonation is propagated through the whole of the nitroglycerin (Désortiaux, Traité sur la Poudre, &c.). Reasoning that the blow of the hammer caused strong compression of the nitroglycerin, and raised its temperature to the exploding point, Nobel was led to try the effect of the blow caused by the detonation in the nitroglycerin of strongly confined detonating mixtures, in the hope that the blow thus given would raise the temperature of the nitroglycerin locally, as was done by the blow of the hammer, and would thereby cause its explosion. He eventually (in 1864) found that the detonation of nitroglycerin could be rendered certain by the use of mercury fulminate contained in a strong copper cap (McRoberts, *l.c.*). This idea of firing an explosive by initial detonation was one of the greatest improvements ever made in the use of explosives. It made the use of nitroglycerin as a blasting agent practicable, was subsequently applied by Abel and Brown to guncotton, and is now used for firing all high explosives.

It has been mentioned that the detonation of nitroglycerin is readily caused when it is subjected to the shock of two hard sonorous bodies, as that of iron on iron. The shock of copper on copper is believed to be less dangerous, and that of wood on wood still less so; but explosions of nitroglycerin have been caused by such shocks (Berthelot, Sur la Force des Matières explosifs, &c.). The sensitiveness of nitroglycerin to friction and percussion increases with the temperature.

Frozen nitroglycerin is less readily detonated by a blow, or by the detonation of mercury fulminate, than when in the liquid state. This was to be expected, as detonation results in both cases from the transformation into heat of the kinetic energy imparted to the particles of nitroglycerin—heat sufficient at the part struck to raise the temperature of the nitroglycerin to the temperature of explosion; and to raise frozen nitroglycerin to that temperature, more heat would be required than in the case of the liquid, on account of the heat absorbed in melting the solid nitroglycerin. Thus, Beckerhinn states (Sitz. W. 72 and 73, in abstract in the Jahresbericht der chemischen Technologie, 1876, 22, 481–487) that quantities of mercury fulminate which would have detonated liquid nitroglycerin with certainty, did not detonate crystallised nitroglycerin; also, that when a flat anvil of Bessemer steel was thinly coated with liquid and with solid nitroglycerin, and a wrought-iron weight allowed to fall on it, the mean height of fall required to effect detonation was for liquid nitroglycerin 0·78 metre (2·6 feet), for frozen nitroglycerin 2·13 metres (7 feet). McRoberts (*l.c.*) states that a detonator containing even so much as 1 gram of mercury fulminate does not effect the detonation of thoroughly frozen nitroglycerin, while 0·1 gram of fulminate will detonate liquid nitroglycerin.

The products of the detonation of nitroglycerin are stated to be those of complete combustion, and the equation representing the change is given as:

$$2C_3H_5(NO_3)_3=6CO_2+5H_2O+6N+O$$

Sarrau and Vieille (Compt. rend. 90, 1060) state that experiment shows that the decomposition of nitroglycerin in a closed vessel is represented by the above equation; but no analysis of the gases is given.

Calculated from the above equation, nitroglycerin contains an excess of 3·52 p.c. oxygen (per 100 nitroglycerin) above that required for complete combustion, and 100 grams of nitroglycerin would be converted into 58·15 grams CO_2, 19·83 grams H_2O, 3·52 grams O, and 18·50 grams N.

Nobel has calculated that 1 vol. of nitroglycerin on explosion generates about 1200 vols. of gases, calculated to normal temperature and pressure, and that the heat generated expands the gases to nearly eight times this volume, and concludes that the explosive force of nitroglycerin is 13 times as great as that of an equal volume of gunpowder.

The quantity of heat evolved by the total combustion of nitroglycerin, as represented in the above equation, is given by Berthelot (Sur la Force des Matières explosifs, &c.), for 227 grams nitroglycerin and in Calories (kgm.-degree units), as follows:—

The water liquid, constant pressure, +356·5 Calories; constant volume, +358·5 Calories.

The water gaseous, constant pressure, +331·1 Calories; constant volume, +335·6 Calories.

Or, per 1 kilogram of nitroglycerin:

The water liquid, constant pressure, +1570 Calories; constant volume, +1579 Calories.

Sarrau and Vieille obtained, by experiment, +1600 Calories.

The volume (at 0° and 0·76 metre pressure) of the gases produced by the detonation of nitroglycerin, calculated from the equation given above, is 714 litres per 1 kilogram nitroglycerin, the water taken as gaseous; or 1142 litres gas (under the given conditions) per 1 litre nitroglycerin. The calculated volume of the permanent gases (*i.e.* the water taken as liquid, tension of aqueous vapour at 0° disregarded) at 0° and 0·76 metre is 467·5 litres per 1 kilogram of nitroglycerin, or 748 litres per 1 litre of nitroglycerin. Berthelot mentions that Sarrau and Vieille found experimentally the volume of permanent gases to be 465 litres at 0° per 1 kilogram nitroglycerin. The gases at the moment of detonation are greatly expanded by the heat of the combustion; according to an early statement of Berthelot (in 1871), the gases are expanded to eight times their volume at 0°.

It will be convenient to requote the numbers obtained by Noble and Abel (Fired Gunpowder, No. 2, Trans. Roy. Soc. 1880) with Waltham Abbey fine-grain gunpowder and ordinary English mining powder.

One kilogram perfectly dry powder gave on explosion:

	W. A. fine-grain	Mining powder
Quantity of heat in Calories (kgm.-degrees) . . .	738·3	516·8
Permanent gases in litres at 0° and 0·76 metre . .	263·1	360·3

The statements as to the relative power of nitroglycerin and ordinary blasting powder as blasting agents vary; partly, no doubt, on account of differences in the rocks blasted, as nitroglycerin is most effective in a compact rock, offering equal resistance in all directions to the gases produced by the explosion. Thus, Trauzl (quoted by Berthelot) stated in 1870 that nitroglycerin used for blasting in quarries produced five to six times the effect of an equal weight of blasting powder; and for equal volumes the difference would be much greater. The effects produced are those of dislocation, specially dependent on the initial pressures. Schwanert (quoted by Böckmann) states that the mean blasting power of nitroglycerin may be taken as being 3·5 to 4 times greater than that of ordinary blasting powder; equal weights being in all probability intended.

The velocity of the propagation of detonation in liquid nitroglycerin has been determined by Abel (Trans. Roy. Soc. 1874, 385, 386). The length of nitroglycerin used was 14 feet, the weight 3 ozs. per foot of the train. The liquid was contained in a V-shaped trough of thin sheet metal; at intervals of 2 feet fine insulated copper wires crossed the trough (having been passed through, and cemented into, small holes in the sides of the trough) sufficiently near the bottom to be covered by the nitroglycerin. The velocities were measured by Noble's chronoscope; the mean rate of detonation was found to be 5305 feet (1612 metres) per second, or little more than one-fourth the rate of detonation of cylinders of compressed guncotton in a continuous row.

Use. – Nitroglycerin, as such, is no longer used as an explosive. It was at one time used to a large extent, especially in America; for instance, about 70 tons of Mowbray's nitroglycerin, transported in the frozen state, was used in the construction of the Hoosac Tunnel in Massachusetts in 1874. Its use was prohibited in England in 1869, and then died out in Europe, but it was employed in America for some years afterwards. Since the invention of nitrogelatin, there is no incentive to use raw nitroglycerin, as the former is as powerful an explosive as the latter.

Dynamites.

It has been already mentioned that the serious accidents which, in 1864 66, attended the transport or manufacture of nitroglycerin were followed by a reaction against its use, and in this country by a prohibitive Act in 1869. To render its transport safe, Nobel introduced the use of a solution of nitroglycerin in wood-spirit (methyl alcohol); a solution which is not explosive, and from which the nitroglycerin was to be separated by precipitation by water at the place where it was to be used. This method of protection was soon abandoned, as the separation of the nitroglycerin was troublesome, and at low temperatures it crystallised out from the solution. A further disadvantage in the use of nitroglycerin is that it may run from the borehole into fissures in the rock, escape detonation, and either burn and give off deleterious oxides of nitrogen, or, if unburned, be a grave source of danger on removing the rock. Attempts were made to overcome this difficulty by lining the borehole with clay. Subsequently Nobel succeeded in making the use of nitroglycerin comparatively safe by employing porous substances to absorb the liquid; to these preparations he gave the name Dynamite.

As he had been experimenting with a mixture of nitroglycerin and gunpowder, Nobel at first used charcoal as an absorbent, and various other substances were subsequently tried, but he found 'kieselguhr,' or so-called infusorial earth, to be the best absorbent of nitroglycerin (Eng. Pat. 1345, 1867). Nobel originally intended that the nitroglycerin should be separated out again for use, but he subsequently found that the dynamite itself could be more readily detonated than the liquid nitroglycerin.

The term 'dynamite' has now a more general significance. It is applied to all mixtures of nitroglycerin with solid substances, which absorb and retain it under ordinary conditions of storage, whatever the nature of the latter; but when used specifically, 'Kieselguhr Dynamite No. 1' is meant.

The absorbent material is known as the 'base' or 'dope,' and dynamites may be classified according to the nature of the base into: (1) those with an inert base; (2) those with a combustible base; and (3) those with an explosive base. The last class includes those with bases which are explosive mixtures (nitrate, chlorate, perchlorate, &c.), and those which are explosive compounds, either of the 'nitro' or 'nitrate' class. In the last class it will be convenient to include blasting gelatin and gelatin-dynamite, although the nitrocelluloses have not yet been considered. Explosive mixtures containing only a small percentage of nitroglycerin, added to increase the ease of detonation, have been classified under the characteristic oxygen salt, but the line of demarcation is not sharp, and the classification is to this extent arbitrary.

The principle of most modern dynamites, which belong to the second and third classes, is to make the base contribute to the energy of the explosive, the nitroglycerin acting as detonating agent to the base. A slight further advantage is obtained in these classes, as the excess of oxygen present in the nitroglycerin is utilised. Nobel first used gunpowder as the explosive base, but safer and more regular results were obtained by replacing the sulphur and charcoal by wood pulp. Wood pulp, owing to its physical properties, has a cushioning effect in preventing accidental detonation by friction or percussion, and gives a certain compressibility to the product which is of advantage in fitting the cartridge in a bore hole. On the other hand, wood pulp renders the dynamites more susceptible to detonating vibrations, and the detonation, once started, proceeds with greater certainty and regularity. This is due to the structure given to the mixture by the pulp, which is sufficiently open and loose for the detonating vibrations to penetrate the mass, and affords a large number of points for molecular attack, whereas an ordinary blow is absorbed by the mass owing to its compressibility. Freezing interferes with the detonation of these mixtures, probably owing to the latent heat of fusion of the nitroglycerin absorbing some of the energy of the detonating wave, but the texture of the dynamite has a very great influence in this connection, the ease of detonation being less affected the more granular and open the texture. Common rosin, used in some of the earlier dynamites, has a slow hardening effect on the mixtures, and in time renders them very insensitive to detonation.

The proportion of nitroglycerin in a dynamite is limited by the possibility of exudation. In the gelatinous dynamites, exudation is prevented by the gelatinisation of the nitroglycerin by solution in it of soluble nitrocellulose. In the lower grades of these explosives wood pulp is an ingredient, and its presence not only permits less complete gelatinisation of the nitroglycerin, but also the use of sufficient nitrate, or other oxidising salt, to give complete combustion without fear of exudation.

Calcium or magnesium carbonate, up to 2 p.c., but usually about 1 p.c., is frequently added to dynamites to act as a stabiliser by neutralising any acid formed by decomposition of the nitroglycerin on storage, and so preventing catalytic acceleration of the decomposition. Zinc or magnesium oxide is also used for the same purpose. Sodium or ammonium carbonate has been, and sometimes still is, used as a stabiliser, but the use of these soluble carbonates is not advisable, owing to their hydrolysing action on the nitroglycerin in the presence of moisture.

1. *Dynamites with an inert base.*

Dynamite No. 1 or Kieselguhr dynamite.—Kieselguhr dynamite contains from 70 to 80 p.c., usually 75 p.c., of nitroglycerin. (Dynamites with less than 30 p.c. of nitroglycerin will not explode.) A small quantity of alkali, formerly 1·5 p.c. ammonium carbonate, now 0·5–1 p.c. anhydrous sodium carbonate, is usually added to neutralise any free acid that may develop on storage; but alkali is not always added.

Kieselguhr. The earth is found in several places; that first used was obtained from Oberlohe in Hanover, where there is an extensive bed of it. It consists of the frustules of diatoms, and is mainly silica; Beckerhinn examined some kieselguhr, and found it to contain 95 p.c. SiO_2, and its specific heat to be 0·2089. The kieselguhr is moderately calcined to remove water and organic matter, then ground and sifted. It should be free from gritty particles. The dried kieselguhr is packed in canvas bags and stored in a dry atmosphere, as it is distinctly hygroscopic. Dynamite made with a guhr containing more than about 0·5 p.c. of water will exude nitroglycerin on storage.

The kieselguhr used at Ardeer is obtained from Aberdeenshire; it absorbs three or four times its weight of nitroglycerin, retaining it under considerable pressure. The calcined material contains about 98 p.c. SiO_2 (McRoberts, *l.c.*).

Manufacture.—The nitroglycerin and kieselguhr are mixed by hand in shallow lead tanks. Any stabiliser is added to the kieselguhr before impregnation. The guhr is weighed out into the tank, the weighed charge of nitroglycerin poured over it from a bucket of indiarubber, guttapercha, or similar material, the ingredients kneaded, and then rubbed through the meshes of a coarse wire sieve, to complete the admixture. Sometimes two sieves are used, a coarse one with about 3 meshes to the inch, and a finer one with 7 meshes to the inch. The dynamite is then in the form of plastic grains. These must neither be dry enough to crumble nor decidedly greasy, or the cartridges will not be satisfactory. If the guhr be too absorbent, the mixture will be too dry for pressing, and in this case a small quantity of barium sulphate is usually added, or, sometimes, mica, talc, or ochre up to 8 p.c. replacing an equal weight of kieselguhr.

The dynamite cartridges are small cylinders, in which form they are squeezed out from the cartridge machine; the latter is a cylindrical metal tube, in which a wooden piston works, pressure being applied to the piston by means of a lever. One end of the tube is terminated by a funnel-shaped piece with orifice of the same diameter as that of the cartridges. The operation is a dangerous one, and every care must be taken to avoid undue friction in the machine, and the paste must never be worked if frozen. The cartridges, usually either $\frac{3}{4}$ or $\frac{7}{8}$ of an inch in diameter, but sometimes 1 inch, are sent out wrapped in parchment or paraffined paper.

Properties.—Kieselguhr dynamite is a plastic, pasty substance, the colour of which varies from pink or grey to a dark-brown, according to the colour of the base, and whether ochre has been added or not. The paste is stiff, or soft and greasy, according to the absorbing power of the kieselguhr. It is slightly compressible, and this property renders it quite safe from detonation by ordinary shocks.

Water separates the nitroglycerin from ordinary kieselguhr dynamite. The specific gravity of dynamite is about 1·6. When unfrozen dynamite is set fire to by application of flame, the nitroglycerin burns quickly with yellowish flame, giving off nitrous fumes. Large quantities can thus be burnt without explosion; but eventually the unburnt portion becomes heated to the temperature of explosion, and explodes. When exposed to a slowly rising temperature, dynamite fires at about 180°. It can be safely destroyed by laying it in a long thin train, pouring any waste oil over the train, and firing it. Dynamite freezes more readily than liquid nitroglycerin, usually at about 4°. Frozen dynamite burns very slowly, thawing preceding combustion. When a comparatively small heap of frozen dynamite cartridges is set fire to, an explosion often ensues. Like nitroglycerin, frozen dynamite is less sensitive to shock than unfrozen, and the ordinary detonator does not explode thoroughly frozen dynamite, although one-tenth part of the detonator charge is sufficient to cause the detonation of unfrozen dynamite (McRoberts, *l.c.*). Since frozen dynamite is comparatively useless as an explosive, it must be thawed or 'tempered' before being used, and this only takes place at temperatures considerably above the freezing-point. Thawing is done in special warming pans, in which the vessel containing the dynamite is surrounded by a jacket containing warm water (at a temperature not above 70°) and this in turn by a layer of felt or other non-conducting material. When a cartridge of dynamite has once been frozen, it has a greater tendency to freeze again without any supercooling. This is probably due to the separation of pure nitroglycerin from its impurities when first frozen, and only very slow readmixture after thawing. Dynamite is less sensitive to shock than nitroglycerin; the sensitiveness increases with the percentage of nitroglycerin in the dynamite, and (like explosives in general) with increase of temperature. It is detonated by the shock of iron on iron, or of iron on stone, but not by that of wood on wood. Dynamite between steel and steel, according to Hess, requires a blow of 0·75 kgm.-metre for detonation; when frozen it requires 1 kgm.-metre. In the unfrozen state it is readily detonated by the shock of a rifle-bullet; Berthelot states that it detonates under the direct blow of the bullet when fired at 50 metres' (164 feet) distance, and even more. Placed on an anvil and struck, it requires a smart blow of the hammer to cause an explosion, and then only the portions directly struck detonate, the rest being scattered without exploding. The silicious skeletons of the frustules of diatoms composing the kieselguhr form separate receptacles for the nitroglycerin, and have a cushioning effect towards a mechanical blow, the energy thereby imparted being divided between the absorbent and the nitroglycerin. Berthelot (Sur la Force des Matières explosifs, &c.) remarks that dynamite is less crushing in its action that nitroglycerin, because the heat evolved on its detonation is shared between the products of the explosion and the inert substance, the latter by its presence lowering the temperature. Thus, the specific heat of kieselguhr (0·2) is almost the same as the mean specific heat of the gaseous products of explosion of nitroglycerin at constant volume; in the case of No. 1 dynamite with 25 p.c. kieselguhr, in a vessel completely filled by it, and too strong to be burst by its detonation, the kieselguhr would lower the temperature of the gases by one-fourth, and consequently diminish the initial pressure. In blasting, the condition of the gases of explosion would be intermediate between constant volume and constant pressure. In using dynamite, its detonation is effected by means of the explosion of a mercury fulminate detonator and fired by an electric current or by means of Bickford fuse, the cap being embedded in the dynamite. The detonator must be sufficiently powerful to ensure complete detonation of the nitroglycerin, or nitrous fumes will be generated in the mine workings. The detonator supplied for the purpose by Nobel's Explosive Company contains about 0·5 gram of a mixture of 70 p.c. mercury fulminate and 30 p.c. potassium chlorate.

The velocity of propagation of the detonation of this dynamite was found by Abel (Trans. Roy. Soc. 1874, 384, 385) to be 20,000 feet per second. The experiment was made with half-inch cartridges of dynamite in a continuous train of 42 feet, the rate being measured at intervals of 6 feet by means of Noble's chronoscope.

Abbot (U.S. Engineers) obtained from his experiments (Report upon a System of Submarine Mines, &c., 1881, 111) the remarkable result that the intensity of action of ordinary kieselguhr dynamite containing 75 p.c. nitroglycerin, fired under water, is greater than that of nitroglycerin. Thus, in a series of experiments he found the intensity of action of nitroglycerin detonated under water to be 81, that of an equal weight of dynamite being 100. To confirm the results, nitroglycerin was mixed, under Abbot's supervision, with prepared kieselguhr into dynamite of 75 p.c., and shots were immediately fired under water with this dynamite, and with the nitroglycerin from which it had been made. The mean of five shots gave the intensity of the liquid nitroglycerin as 85, that of the dynamite being 100 (equal weights compared). Abbot remarks that in blasting hard rock, nitroglycerin is admitted to be by far stronger than dynamite; in explanation he supposes that in dynamite the particles of kieselguhr slightly retard chemical action, and that the resistance opposed by water, being of a slightly yielding character, may exact more time than is required by pure nitroglycerin. According to Abel's experiments, however, the rate of detonation of dynamite is very much quicker than that of liquid nitroglycerin,—a result agreeing with those of Abbot's experiments, but not with his explanation of them. It is true, as Abel points out, that the determination of the rate of detonation of liquid nitroglycerin (which was contained in an open trough) was likely to be given too low, owing to the tendency of the liquid particles to escape from the blow of the detonation, and that experiments with *confined* nitroglycerin would be desirable.

Tested by the lead cylinder method, the intensity of action of nitroglycerin is 1·4 when that of No. 1 dynamite is unity. Von Pischoff, in Austria in 1869, comparing the relative values of dynamite and gunpowder, found that the former was roughly three times as strong as gunpowder, variations from 2·4 to 3·3 being obtained according to the nature of the rock. The nature of the kieselguhr has some influence on the explosive power of the dynamite; the guhrs containing most tubular structures not only absorb better, but each of these tubes offers resistance on detonation, and confers greater intensity of action by its tamping effect.

Dynamite of Vonges.—Instead of kieselguhr, in France a similar silicious earth called *Randanite* (from Randan in the Puy-de-Dôme) is used as the absorbent in the Vonges make of dynamite. Tripoli and the ashes of Boghead coal have also there been employed as substitutes for kieselguhr. Analysis of a modern sample gave 75 p.c. nitroglycerin, 20·8 p.c. randanite, 3·8 p.c. quartz, and 0·4 p.c. magnesium carbonate. More rarely *Dynamites Nos.* 2 and 3 are used in France, containing 35 and 25 p.c. nitroglycerin respectively. The American *Giant powder No.* 1 is dynamite No. 1 containing 0·5 p.c. sodium carbonate.

Magnesia alba has also been used as the absorbent of nitroglycerin, its absorptive power being said to exceed that of kieselguhr, and it is also said to increase the intensity of action of the dynamite by the expulsion of its carbon dioxide. The combination was proposed in 1879, by Jones of Caerphilly, and named *Nitromagnite* or *Dynamagnite*. Its manufacture was abandoned, as it was decided that it conflicted with the existing patents of Nobel.

Modifications of kieselguhr dynamite have been proposed, more especially on the Continent, with a view of rendering it safe to use in fiery mines: various additions, such as salts containing much water of crystallisation, being made to reduce the temperature of the flame. Such explosives are naturally less powerful than ordinary dynamite.

In *Wetter dynamite*, proposed by Müller of the Cologne dynamite factory (Eng. Pat. 12424, 1887), crystallised sodium carbonate is used. Composition 52 p.c. nitroglycerin, 14 p.c. kieselguhr, and 34 p.c. soda crystals.

Grisoutite contains magnesium sulphate. It is composed of 53 p.c. nitroglycerin, 14·5 p.c. kieselguhr, and 32·5 p.c. magnesium sulphate.

Nobel Ardeer powder is a dynamite of this class, for although it contains nitre, it has no added combustible. Composition: 33 p.c. nitroglycerin, 40 p.c. magnesium sulphate, 13 p.c. kieselguhr, and 5 p.c. nitre.

Mica powder (Abbot, Report upon a System of Submarine Mines, &c., 93, 110) consists of finely divided mica scales and nitroglycerin. It was made in the United States by Mowbray, and was largely used, with good results, in completing the Hoosac Tunnel. The nitroglycerin adheres to the scales, but is not absorbed by them. Mowbray claimed that, owing to the very large surface exposed, a more instantaneous reaction is secured than with liquid nitroglycerin. He estimates the interstitial spaces at one-fourth the volume of the powder when tolerably well rammed.

Abbot experimented with a No. 1 mica powder containing 52 p.c. nitroglycerin, and with a No. 2 containing 40 p.c.; the charges being detonated under water. He found the intensity of action of No. 1 to be 83, of No. 2 to be 62; that of liquid nitroglycerin, in the same circumstances, being 81, and that of kieselguhr dynamite No. 1, containing 75 p.c. nitroglycerin, being 100 (equal weights compared). The result is remarkable, as it gives the intensity of action of the nitroglycerin in mica powder as double that of an equal weight of liquid nitroglycerin.

2. *Dynamites with a Combustible Base.*

In this class the explosive power of the nitroglycerin is enhanced by the utilisation of its excess of oxygen for combustion of part of the base. There is, however, a considerable excess of combustible matter, leading to the formation of carbon monoxide on detonation, and the dynamites containing an oxygen salt in addition are more usual.

Cork charcoal is very absorptive but costly, and the more usual combustible absorbents are wood meal, flour, and starch.

Carbodynamite is a preparation introduced by Messrs. W. D. Borland and W. F. Reid (Eng. Pat. 758, 1886). It consists of 10 p.c. cork charcoal, which has absorbed 90 p.c. nitroglycerin. Sodium or ammonium carbonates and water may or may not be present.

It is claimed for carbodynamite that it can be kept under water for weeks without losing its nitroglycerin, which would be a great advantage over kieselguhr dynamite.

As was to be expected from the high percentage of nitroglycerin, the intensity of action of carbodynamite is very high—much higher than that of kieselguhr dynamite. In one variety of carbodynamite, water was added to render the explosive safe enough to use in fiery mines. Another variety, No. 2, belongs to the third class of dynamites, as it contains 80 p.c. nitroglycerin, 14 p.c. nitre, and 6 p.c. cork charcoal.

Grisoutite.—Another form of this safety explosive contains wood meal as the absorbent, instead of kieselguhr. Composition: 44 p.c. nitroglycerin, 12 p.c. wood meal, 44 p.c. magnesium sulphate. This explosive is on the Belgian permitted list. Another explosive of this class on the same list is *Dynamite antigrisouteuse V*, which has the same composition except that sodium sulphate replaces the magnesium sulphate as restrainer and temperature reducer. The limit charge of the former is 300 grams, and of the latter 650 grams.

Forcite is the name given to explosives manufactured in various grades by the American Forcite Company, New Jersey. The original patent (of 1881) describes forcite as consisting of nitroglycerin incorporated with unnitrated gelatinised cellulose and with nitre. Cotton or other form of cellulose was to be purified chemically as in paper making, to be reduced to powder and to be subjected to the action of high-pressure steam, by which it was converted into a gelatinous mass. It was then allowed to cool, and was to be incorporated at 40° with nitroglycerin and with nitre. One of the best compositions was stated to be: nitroglycerin, 75 p.c.; gelatinised cotton, 7 p.c.; nitre, 18 p.c. Dextrin and ordinary cellulose in powder might partly replace the gelatinised cotton.

Forcite is described as a hard plastic substance, having very much the appearance and toughness of indiarubber. Economy, non-exudation of nitroglycerin, and imperviousness to water, were claimed for it. There is considerable variation in the statements as to the composition of forcite; thus, in one kind the gelatinised nitroglycerin is said to be incorporated with a mixture composed of sodium nitrate, wood tar, a little sulphur and wood pulp. It is made in various grades containing different amounts of nitroglycerin. Eissler states that the type mostly in use (in the United States, and in 1886), and which possesses the best qualities, is the No. 1, containing from 65 to 85 p.c. nitroglycerin; also that the quantity of nitroglycerin in different grades varies from the large amount mentioned to only 20–25 p.c. He states that quadruple-force caps are employed to explode forcite.

Abbot (U.S. Engineers) made estimations of the intensity of forcite exploded under water; the intensity varied with the grade, between 88 and 133, ordinary kieselguhr dynamite No. 1 being 100 (Addendum II. to Report on Submarine Mines). Belgian and other continental makes of forcite contain nitrocellulose, and come in class 3 of dynamites.

Forcite antigrisouteuse No. 2 has a similar composition to 'grisoutite.'

Rhenish dynamite consists of 75 p.c. of a solution of naphthalene in nitroglycerin, 25 p.c. of kieselguhr, and a little chalk or barium sulphate.

3. *Dynamites with an Explosive Base.*

Kieselguhr dynamite is much too violent and local in its effects to be used in most mining operations, such as in coal-mines or slate and granite quarries, where great power and shattering effects are undesirable. As the force cannot be moderated by reducing the proportion of nitroglycerin without increasing the difficulty of detonation, the dynamites with an explosive base have gradually superseded it for mining purposes.

i. *Dynamites with a Potassium Nitrate Mixture Base.*

In many of these mixtures the proportion of combustible matter is so high that a large proportion of the carbon is only oxidised to monoxide on detonation. This is objectionable in explosives to be used in mines. The paper wrapper of the cartridge has also to be considered as combustible matter in this connection.

Dynamite No. 2 is black in colour, and is milder and slower in its action than No. 1. It was introduced to imitate the explosive characteristics of gunpowder. It consists of (not more than) 18 p.c. of nitroglycerin, uniformly mixed with 82 p.c. of a pulverised preparation, composed of 71 p.c. potassium nitrate, 10 p.c.

charcoal, 1 p.c. paraffin. Scarcely used at all in this country.

Dynamite No. 3 was intermediate in power between No. 1 and No. 2. It consisted of a mixture of equal parts of No. 1 and a mixture of potassium nitrate and wood meal.

Britonite No. 2, an English permitted explosive, contains on the average 24 p.c. nitroglycerin, 30 p.c. potassium nitrate, 38 p.c. wood meal, and 8 p.c. ammonium oxalate. Limit charge 24 ozs., pendulum swing 2·26 inches.

Rend rock is a modern modification of 'Lithofracteur,' having the composition 40 p.c. nitroglycerin, 40 p.c. nitre, 13 p.c. wood pulp, and 7 p.c. pitch.

Atlas powders B+ and C+, as used in the construction of the Panama Canal, contained *B+*, 60 p.c. nitroglycerin, with wood pulp and nitre, and 3 p.c. of magnesia; *C+*, 45 p.c. nitroglycerin, with wood pulp and nitre and 2 p.c. of chalk.

Some forms of *Wetter dynamite* contain a similar mixture. A sample from Wittenberg contained 25 p.c. nitroglycerin, 35 p.c. mixed nitrates of potassium and barium, and 40 p.c. wood meal.

Cambrite, on the English authorised list, contains 22–24 p.c. nitroglycerin, 26–29 p.c. potassium nitrate, 3–4·5 p.c. barium nitrate, 32–35 p.c. wood meal, 0–0·5 p.c. calcium carbonate, 7–9 p.c. ammonium oxalate, and 3·5–6 p.c. moisture. Limit charge 30 ozs., pendulum swing 1·98 inches, No. 6 detonator.

Carbite, a French dynamite of this class, contains 25 p.c. nitroglycerin, 34 p.c. potassium nitrate, 1 p.c. barium nitrate, 38·5 p.c. flour, 1 p.c. powdered bark, and 0·5 p.c. sodium carbonate.

Carbonite, made by Bichel and Schmidt of Schlebusch, one of the first and most successful of safety explosives for use in fiery mines. It contains 25–27 p.c. nitroglycerin, 30–36 p.c. of a mixture of potassium and barium nitrates, and 40–43 p.c. starch and wood meal, with 0·5 p.c. sodium carbonate, and 0·5 p.c. of sulphuretted benzene. An actual sample contained 25 p.c. nitroglycerin, 34 p.c. potassium nitrate, 1 p.c. barium nitrate, 10 p.c. wood meal, 29·5 p.c. rye flour, and 0·5 p.c. sodium carbonate.

Kolax, an English permitted explosive, contains on the average 25 p.c. nitroglycerin, 26 p.c. potassium nitrate, 5 p.c. barium nitrate, 34 p.c. wood meal, and 10 p.c. starch.

Super-Kolax is of similar composition, but to enable it to pass the severer Rotherham test, about 10 p.c. of the explosive base is replaced by ammonium oxalate.

Pit-ite No. 2, on the English permitted list, contains 23–25 p.c. nitroglycerin, 28–31 p.c. potassium nitrate, 33–36 p.c. wood meal, 7–9 p.c. ammonium oxalate, and 2·5–5 p.c. water. Limit charge 32 ozs., pendulum swing 2·15 inches, detonator No. 6.

Stonite, also made by Bichel and Schmidt, consists of 68 p.c. nitroglycerin, 20 p.c. kieselguhr, 8 p.c. potassium nitrate, and 4 p.c. wood meal.

Tutol, on the English permitted list, contains on the average 25 p.c. nitroglycerin, 33 p.c. potassium nitrate, 2 p.c. barium nitrate, 40 p.c. wood meal, and up to 0·5 p.c. sodium bicarbonate.

Kynite is a safety explosive of similar composition to carbonite. One analysed sample contained 25 p.c. nitroglycerin, 35 p.c. barium and potassium nitrates, and 40 p.c. starch and wood meal. As licensed, *Kynite condensed* contains 24–26 p.c. nitroglycerin, 32·5–35 p.c. starch, 2·5–3·5 p.c. wood meal, 31·5–34·5 p.c. barium nitrate, and 0–0·5 p.c. calcium carbonate; the explosive to be used only in a non-waterproofed parchment-paper wrapper.

Kohlen-carbonite, a Belgian permitted explosive, contains on the average 25 p.c. nitroglycerin, 34 p.c. potassium nitrate, 1 p.c. barium nitrate, 38·5 p.c. flour, 1 p.c. tan meal, and 0·5 p.c. sodium carbonate. Limit charge 900 grams.

Minite is a similar explosive without the barium nitrate and tan meal.

Dualine contains 50 p.c. nitroglycerin, 20 p.c. potassium nitrate, and 30 p.c. sawdust.

II. *Dynamites with a Sodium Nitrate Mixture Base*

The dynamites of this class, like those with an ammonium nitrate base, are hygroscopic. Under damp atmospheric conditions the nitrate deliquesces, and its solution displaces the nitroglycerin, and causes it to exude These dynamites are consequently liable to become dangerous, and although largely used elsewhere, were for a long time not licensed in England. Several examples both of this and the ammonium nitrate class have, however, recently been permitted.

Judson powder is an explosive which has been largely used in the United States in quarrying and railway work; it is a roughly made sodium nitrate blasting powder, the grains of which are coated with nitroglycerin. The grade R.R.P. is the one most commonly used, and is sold at the price of common saltpetre blasting powder; it is composed of sodium nitrate 64 p.c., sulphur 16 p.c., cannel coal 15 p.c., nitroglycerin 5 p.c. The nitrate, sulphur, and coal are thoroughly mixed in fine powder, and the mixture heated on a pan by steam under pressure, and constantly stirred until the sulphur melts. The mass is then allowed to cool, when it is found agglomerated in grains, which are sorted by sieves and coated with nitroglycerin by stirring. The object of coating the powder grains with the nitroglycerin was to promote the quickness of explosion. It is exploded by the detonation of a primer of Giant or Atlas powder. These low-grade dynamites are readily detonated even in the coldest weather, probably owing to their loose and open texture. Abbot (*v. supra*) found the intensity of action of the R.R.P. grade, exploded under water, to be 38–39, kieselguhr dynamite No. 1 being 100. Other brands now in use with their percentages of nitroglycerin are: F. 10 p.c., F.F. 15 p.c., F.F.F. 20 p.c., Dbl. Ex. 27 p.c., and Tpl. Ex. 33 p.c.

Giant powder No. 2, supplied by the Atlantic Giant Powder Company, and composed of nitroglycerin 36 p.c., potassium or sodium nitrate 48 p.c., sulphur 8 p.c., resin, powdered coal or charcoal 8 p.c. Exploded under water, its intensity of action was 83 p.c. of that of dynamite No. 1. A more modern composition

8 p.c. kieselguhr, and 6 p.c. sulphur. There are six or more other brands with percentages of nitroglycerin varying from 20 to 50.

Vigorite contains 30 p.c. nitroglycerin, 60 p.c. sodium nitrate, 5 p.c. charcoal, and 5 p.c. sawdust.

Vulcan powder was used in some of the earlier blasting work at Hellgate, New York Harbour. The usual trade explosive, of the composition nitroglycerin 30 p.c., sodium nitrate 52·5 p.c., charcoal 10·5 p.c., sulphur 7 p.c., fired under water gave intensity = 78 p.c.; and a No. 2 sample containing 35 p.c. nitroglycerin, gave intensity = 82 p.c. compared with the usual standard (Abbot).

Lithofracteur, invented by Engels, and made by Krebs & Co., of Cologne, is said to consist of 55 p.c. nitroglycerin, 21 p.c. kieselguhr, and 24 p.c. of charcoal (bran or sawdust), barium nitrate, bicarbonate of soda, peroxide of manganese, and sulphur; the latter ingredients in such proportion as to give the highest temperature and greatest quantity of gas.' Stated to be nearly equal in intensity to kieselguhr dynamite No. I (Böckmann, Die explosiven Stoffe). One sample gave on analysis 52 p.c. nitroglycerin, 30 p.c. kieselguhr, 12 p.c. powdered coal, 4 p.c. sodium nitrate, and 2 p.c. sulphur; another sample contained 70 p.c. nitroglycerin, 23 p.c. kieselguhr, 2 p.c. powdered coal, and 5 p.c. barium nitrate. This explosive was formerly on the list of 'authorised' explosives, but is not now used in this country.

Lignin dynamites. In the United States, large quantities of nitroglycerin preparations are used in rock-blasting, consisting of nitroglycerin absorbed by a mixture of wood pulp (or of sawdust in some of the lower grades) and a nitrate, usually sodium nitrate. For the complete combustion of wood with formation of sodium carbonate, about 2·5 parts by weight of sodium nitrate are required to 1 of wood. General Abbot, in 1885, says, 'Development in the United States is at present most actively directed to the dynamites with explosive bases, economy being sought in making use of the least possible percentage of nitroglycerin.' At the present time these dynamites are very largely used under the name *Straight Dynamites.* They are graded as of 10 p.c., 15 p.c., 20 p.c., &c., up to 75 p.c. strength, according to the percentage of nitroglycerin they contain, but the actual nitroglycerin content frequently varies to a considerable extent from the nominal. The sodium nitrate content varies from about 16 to 64 p.c., the wood pulp from 8 to 20 p.c., and the moisture from 1 to 3 p.c. Calcium or magnesium carbonate is usually present to the extent of about 1 to 2 p.c. For the lower grades the combustible matter frequently contains flour and sulphur in addition to the wood pulp, but sulphur is objectionable in dynamites to be used underground, owing to the sulphur dioxide present in the products of explosion. Their velocity of detonation varies with the percentage of nitroglycerin, being, in metres per second, about 2100 for the 10 p.c., 4200 for the 30 p.c., 4800 for the 40 p.c., and 6200 for the 75 p.c.

Lignin dynamites are largely manufactured by the Cape Explosives Works and used in South Africa under the name *Ligdyns.* They can be detonated with a No. 5, 0·8 gram, detonator, and this apparently brings out their full power; but it is more usual to use a No. 6, 1·0 gram, detonator, as the action is then more certain. The ligdyns can still be detonated when frozen, but their full force is not attained.

Atlas powder may be taken as a type of several American preparations. It consists essentially of sodium nitrate, wood pulp (or sometimes of sawdust), magnesium carbonate, and nitroglycerin. A series of grades is made, containing 75 p.c. to 20 p.c. nitroglycerin.

Abbot experimented with two grades, A and B, of Atlas powder; they were composed of:

	Grade A	Grade B
Sodium nitrate . .	2	34
Wood fibre . . .	21	14
Magnesium carbonate .	2	2
Nitroglycerin . .	75	50

Fired under water, the intensity of grade A was just that of an equal weight of kieselguhr dynamite No. 1 (75 p.c. nitroglycerin); whilst the intensity of Atlas B was = 99 p.c. of the same standard (Abbot, Addendum II. to Report on Submarine Mines). Grade A shows no economy in nitroglycerin over kieselguhr dynamite of the same percentage, probably owing to the too low ratio of sodium nitrate to wood fibre. Grade B, in which the ratio of nitrate to wood is that of complete combustion, shows a great economy in nitroglycerin.

Abel found (by the lead cylinder method) the intensity of an Atlas powder of American make to be 106, kieselguhr dynamite No. 1 being = 100.

Hercules powder has essentially the same composition as Atlas powder. Several grades of it are made in the United States, containing from 75 p.c. to 20 p.c. nitroglycerin. Some years since, two grades were tried by Abbot, and fired under water; their composition and intensity of action were:

	No. 1	No. 2
Nitroglycerin . .	77 p.c.	42·0 p.c.
Sodium nitrate . .	1 „	43·5 „
Wood pulp . .	2 „	11·0 „
Magnesium carbonate .	20 „	3·5 „
Intensity . .	106	83·0

(Kieselguhr dynamite No. 1 being = 100).

Similar American lignin dynamites of this class are the various *Giant powders*, with quantities of nitroglycerin, varying from 20–50 p.c. (exclusive of the giant powders 1 and 2 already mentioned); *Safety nitro powder*, containing 69 p.c. nitroglycerin, 18 p.c. sodium nitrate, and 13 p.c. wood pulp; *Hecla powder*, made in seven grades, containing 75–20 p.c. nitroglycerin; *Miner's friend*, and others.

Rhexite is manufactured by the Borkenstein Co. in Styria. One sample contained 64 p.c. nitroglycerin, 18 p.c. sodium nitrate, [illegible] p.c. decayed wood, and 7 p.c. wood meal.

Rexite as licensed by the Home Office, the explosive contains 64–68 p.c. ammonium nitrate, 13–16 p.c. sodium nitrate, 6·5–8·5 nitroglycerin, 6·5–8·5 trinitrotoluene, 3–5 p.c. wood meal, and 0·5–1·5 p.c. moisture, used in a stout paper case waterproofed with ceresin and wax.

Tutol No. 2 is a variety of this explosive containing sodium nitrate instead of potassium nitrate, and in which about 12 p.c. of the explosive base is replaced by sodium chloride.

Some forms of *Carbonite* contain sodium nitrate instead of nitre. *Coal carbonites I. and II.* contain respectively 25 and 30 p.c. nitroglycerin, 30·5 and 24·5 p.c. sodium nitrate, 39·5 and 40·5 p.c. rye flour (containing about 2·5 p.c. water), and 5 and 5 p.c. potassium dichromate. *Carbonite I.A* contains sodium chloride instead of potassium dichromate.

Phœnix powders resemble the above forms of carbonite. They are manufactured in various brands :

	I.	II	III
Nitroglycerin . .	30	25	25
Sodium nitrate . .	30	1	35
Barium and potassium nitrates . . .	—	34	—
Rye flour . . .	40	—	40
Wood meal . . .	—	40	—
	100	100	100

Sometimes a little nitrocotton is added to gelatinise the nitroglycerin.

iii. *Dynamites with an Ammonium Nitrate Mixture Base.*

Ammonia dynamite was a nitroglycerin preparation proposed and patented in 1872 by Ohlson and Norrbin, which consisted of nitroglycerin 10 p.c. to 20 p.c., ammonium nitrate 80 p.c., charcoal 6 p.c. The material is deliquescent, and paraffin was added to the mixture to waterproof it. Berthelot states that practical tests have shown ordinary dynamite of 60 p.c. nitroglycerin, and the preparation consisting of 75 p.c. ammonium nitrate, 3 p.c. charcoal, 4 p.c. paraffin, and 18 p.c. nitroglycerin, to be approximately equal in intensity of action.

In 1873 the British Dynamite Co. (now Nobel's Explosive Co.) submitted two samples of ammonia dynamite to the special War Office Committee on Guncotton, &c., containing respectively 18 and 13 p.c. nitroglycerin, 75 and 70 p.c. ammonium nitrate, 4 and 7 p.c. paraffin, and 3 and 10 p.c. charcoal dust. They were unfavourably reported on, on account of the possibility of exudation of nitroglycerin on storage, due to the deliquescent nature of the ammonium nitrate. As permitted for manufacture in this country, Nobel's ammonia powder had the composition :

	No. 1	No. 2
Ammonium nitrate .	82–86 p.c.	78–82 p.c
Nitroglycerin . .	7–9 ,,	9–11 ,,
Wood meal . .	6–8 ,,	8–10 ,,
Moisture . .	0·5–2 ,,	0 5–2·5 ,,

A recent sample of *Pulverulent ammonium dynamite* contained 20 p.c. nitroglycerin, 25 p.c. ammonium nitrate, 36 p.c. sodium nitrate, and 19 p.c. dry rye flour.

'Ammonia dynamites,' in which part of the nitroglycerin in the earlier lignin dynamites is replaced by ammonium nitrate, are used to some extent in the United States. They are graded in per cent. strengths like the more usual simple nitroglycerin mixtures. The nitroglycerin and ammonium nitrate are present in roughly equal proportions, and the sum of their percentages corresponds to the grade strength in the lower grades, but in the higher grades their combined percentages are somewhat higher than that of nitroglycerin in the 'straight dynamites,' so as to give comparable strengths. Their velocities of detonation increase with the strength, but, as would be expected, are lower than those of the corresponding 'straight dynamites.' According to Comey, the velocity of detonation of the 30 p.c. grade is about 3500, the 40 p.c. about 4100, and the 50 p.c. about 4400 metres per second. His result for the 60 p.c. strength was anomalous, being only 3000 metres per second.

Du Pont Permissible No. 1, manufactured in the United States and on the English permitted list, contains 9 p.c. nitroglycerin, 68 p.c. ammonium nitrate, 8 p.c. wood pulp, and 15 p.c. sodium chloride. Limit charge 18 ozs., pendulum swing 2·82 inches.

Haylite No. 3, manufactured by the National Explosives Co., and also on the permitted list, contains approximately 9·5 p.c. nitroglycerin, 60 p.c. ammonium nitrate, 5 p.c. wood meal, 19·5 p.c. sodium chloride, 5 p.c. ammonium oxalate, and 1 p.c. moisture. Limit charge 16 ozs., pendulum swing 2·44 inches.

Most modern dynamites containing ammonium nitrate also contain nitrocotton, which serves to protect them from the action of moisture.

iv. *Dynamites with a Barium Nitrate Mixture Base.*

Some dynamites, for example, 'Haylite No. 1,' 'Kolax,' and 'Tutol,' contain barium nitrate in admixture with other oxygen salts in their base.

Nitro Densite is an English permitted explosive containing 17–19 p.c. nitroglycerin, 24–26 p.c. barium nitrate, 4–6 p.c. wood meal, 24–27 p.c. starch, 22–24 p.c. Franch chalk, and 2–5 p.c. moisture. Limit charge 28 ozs., pendulum swing 1·47 inches, detonator No. 6.

v. *Dynamites with a Chlorate Mixture Base.*

Although the substitution of a chlorate for a nitrate mixture, as an absorbent for nitroglycerin, increases the power of the resultant explosive, it adds to the cost, and the explosives possess the dangerous properties inherent in chlorate mixtures. They are not used in this country.

An early example of this class of dynamite was proposed by Horsley, in 1872, in which a mixture of finely ground gall nuts and potassium chlorate, in the proportion of 1 to 3, was impregnated with 20 p.c. nitroglycerin.

Some modern grades of the American *Hercules powders* contain potassium chlorate and sugar instead of the older wood pulp, their composition being: 40–75 p.c. nitroglycerin, 1–16 p.c. sugar, 1–3·5 p.c. potassium chlorate, 2–30 p.c. potassium nitrate, and 10–20 p.c. magnesium carbonate.

vi. *Dynamites with a Perchlorate Mixture Base.*

Several explosives containing a considerable proportion of nitroglycerin, partly gelatinised with a small quantity of soluble nitrocotton, and with a mixture of potassium perchlorate and wood meal as a base, have during the last few years passed the English tests and have been placed on the list of permitted explosives. These have been classified separately, as they characterised by the perchlorate, though y also belong to Class VIII.

Ammonium oxalate is present as a cooling nt instead of the previously more common monium nitrate, and this obviates the fault hygroscopicity. The small proportion of rohydrocarbon frequently present is not ended primarily as a combustible, but is ded to lower the freezing-point of the nitro-ycerin.

The method of manufacture is to first sift e perchlorate, oxalate, and wood meal, the o former through a 50–100-mesh sieve, the tter through a 20–50-mesh sieve, roughly mix em by hand in a pan, then to pour over the ixture the partially gelatinised nitroglycerin, nd again roughly mix. The final incorporation carried out in a nitrogelatine incorporator at temperature not above 30°.

Ajax powder contains on the average 22·5 .c. nitroglycerin, 0·8 p.c. soluble nitrocotton, 7·2 p.c. potassium perchlorate, 25 p.c. ammonium oxalate, 11 p.c. wood meal, and 3·5 p.c. i- or tri-nitrotoluene. Limit charge 12 ozs., endulum swing 2·69 inches.

Dynobel, manufactured by Nobel's Explosives Co., contains 31·5–33·5 p.c. nitroglycerin, ·5–1 p.c. collodion cotton, 26–28 p.c. potassium erchlorate, 28·5–30·5 p.c. ammonium oxalate, ·5–10·5 p.c. wood meal, and 0–1·5 p.c. moisture. imit charge 22 ozs., pendulum swing 2·61 nches, detonator No. 6.

Neonal is manufactured by the New Explosives Co. in two varieties. *Neonal* contains 0–22 p.c. nitroglycerin, 0·5–1·5 p.c. collodion-otton, 36–38 p.c. potassium perchlorate, 24–26 .c. ammonium oxalate, 14–16 p.c. wood meal, –0·4 p.c. di- or tri-nitrotoluene, and 0–2 p.c. noisture. Limit charge 16 ozs., pendulum wing 2·56 inches, detonator No. 6; and *Neonal No.* 1 contains 40 p.c. nitroglycerin, ·8 p.c. collodion cotton, 14 p.c. potassium per-hlorate, 39 p.c. ammonium oxalate, and 5 p.c. wood meal. Limit charge 30 ozs., pendulum wing 2·51 inches.

Swale powder is, on the average, a mixture of 19 p.c. nitroglycerin, 1 p.c. soluble nitrocotton, 7·5 p.c. potassium perchlorate, 10·5 p.c. wood meal, 28 p.c. ammonium oxalate, and 4 p.c. i- or tri-nitrotoluene. Limit charge 20 ozs., endulum swing 2·50 inches.

vii. *Dynamites containing a Nitro Derivative.*

Castellanos powder was an early dynamite f this class which contained nitroglycerin, itrobenzene, fibrous material, and kieselguhr. It was claimed to burn easily and rapidly without xplosion, and to be less liable to freeze than rdinary dynamite.

Many dynamites contain a small proportion of nitrohydrocarbon, added simply for the purpose of reducing the freezing-point of the nitroglycerin.

Rexite, already mentioned, contains tri-nitrotoluene.

Melling powder, an explosive on the English permitted list, contains 4–6 p.c. nitroglycerin, 5–7 p.c. trinitrotoluene, 51–55 p.c. ammonium nitrate, 11–13 p.c. sodium nitrate, 3–5 p.c. wood meal, 18–20 p.c. ammonium oxalate, and up to 2 p.c. moisture. Limit charge 12 ozs., pendulum swing 2·62 inches, detonator No. 6.

Antigel de Sûreté, on the Belgian permitted list, contains 25 p.c. nitroglycerin and 15 p.c. dinitrotoluene, with sodium nitrate, wood meal, and a little ammonium sulphate.

viii. *Dynamites containing Nitric Esters.*

The nitric ester almost invariably used is soluble nitrocotton.

Blasting gelatin. Owing to the tendency of nitroglycerin to exude from the dynamites containing a base of either kieselguhr or an explosive mixture, Nobel continually experimented in the direction of thickening the nitroglycerin by dissolving some substance in it; preferably an explosive. He tried guncotton as early as 1867, but it was not until accident led him, in 1875, to try collodion with the assistance of a solvent, that the problem was solved. He found that 7–8 p.c. of collodion cotton could be dissolved in nitroglycerin to form a plastic jelly which was impervious to water (Fr. Pat. 106384; Eng. Pat. 4179, 1875). Subsequently, Nobel found that warm nitroglycerin would itself dissolve the collodion cotton without the assistance of a solvent. The resulting explosive was known as 'blasting gelatin' or 'nitrogelatin.' It has been mentioned that nitroglycerin contains an excess of 3·52 p.c. of oxygen above that required for the complete combustion of the carbon and hydrogen of the nitroglycerin; this oxygen is utilised in effecting the complete combustion of the nitrocotton, itself deficient in oxygen. The composition is consequently most powerful, and it is also proof against the action of water. For the purpose of blasting hard rock, this class of dynamite has now practically displaced the previous types of dynamite in England and most continental countries.

Composition.—The relative proportions of the two ingredients vary somewhat. Blasting gelatin was first experimented with on the large scale in Austria, and the usual proportion there is 7 p.c. nitrocotton to 93 p.c. nitroglycerin. The same proportions are used in Germany. In England and Switzerland, the nitrocotton varies between 5 and 10 p.c., usually about 7 p.c. With only 4 p.c. nitrocotton the resultant product is a thin liquid jelly. In Italy 8 parts of nitrocotton are dissolved in 90 parts of nitroglycerin, with the aid of methyl alcohol.

The nitrocotton used is the so-called collodion cotton or soluble nitrocellulose, which should be as dry and as free from insoluble nitrocotton as possible. It should have as high a nitrogen content as is compatible with complete solubility in nitroglycerin. The nitrocotton, for this purpose, requires very special preparation, and even now the conditions are not perfectly understood for the preparation of a nitrocotton fulfilling the above requirements, and also giving a perfectly stiff and dry blasting gelatin, that will not exude nitroglycerin when stored in hot climates. A nitrocotton of the correct type is, however, essential: stiffening by the addition of more nitrocotton of a poor quality is of no value, as the gelatin resulting, though hard when first manufactured, rapidly deteriorates, and exudes nitroglycerin on storage, especially in hot climates. It is frequently stabilised by the addition of up to 2 p.c. of calcium or magnesium carbonate. A very small quantity of mineral jelly is sometimes added for the same purpose.

Manufacture.—In the preparation of small quantities, the weighed charge of nitroglycerin is introduced into a square, jacketed copper or lead trough, heated by the circulation of hot water. When the nitroglycerin is hot, the charge of finely divided and thoroughly dried collodion cotton is gradually added, the mixture being stirred with a wooden paddle from time to time for 2 hours until the gelatinisation is complete and the jelly in the tanks is semi-transparent. The mass is then kneaded by hand until perfectly uniform. By using mechanically worked wooden paddles revolving very slowly, a charge of 2 cwts. of the explosive can be thoroughly gelatinised in about 1 hour. The temperature of the nitroglycerin is usually kept between 35° and 40°; occasionally, temperatures approaching 45°–50° are used, but the operation becomes very dangerous at the higher temperature, and this is only used under exceptional circumstances, when the solution of the nitrocotton is sluggish, usually due to the nitrocotton being damp.

On a larger scale, the kneading is done mechanically. The apparatus in use at Ardeer at the time is described by McRoberts in a paper read before the Society of Chemical Industry in May, 1890 (J. Soc. Chem. Ind. 1890, 267), but most factories now use the 'nitro-universal incorporator' kneading machines of Werner, Pfleiderer, and Perkins, such as are used in the manufacture of smokeless powders (*q.v.*).

The use of a solvent such as methyl alcohol, ethyl alcohol, acetone, or acetic ether does away with the necessity for heat in the process, and also renders the explosive less sensitive and less liable to freeze, but the explosive power of the product is also lowered and the addition is not usual.

The gelatin paste whilst still warm is finally worked into cartridges by some form of Archimedean-screw machine, the mass being too stiff for the presses used for ordinary dynamite, such as that described by McRoberts (*l.c.*), the resulting rod of gelatin being cut across by bronze knives into cylinders of the requisite length, 3–4 inches, and wrapped in parchment- or paraffined paper.

Cooking and Kynoch, Ltd. (Eng. Pat. 28178, 1911), manufacture blasting gelatin from wet nitrocotton, containing 20–30 p.c. water, by mixing with the nitroglycerin at a temperature of 40°–60°. The water is driven off by drawing the product to and fro between two chambers through narrow-diameter jacketed tubes heated to the desired temperature.

Properties.—Blasting gelatin is a translucent, elastic semi-solid of light-yellow colour and of sp.gr. 1·55 to 1·59. It does not deteriorate by submergence in water, though it becomes paler in colour and more opaque, water not separating the nitroglycerin—an advantage over kieselguhr dynamite No. 1. It freezes at low temperatures; but while some cartridges freeze readily at about 2° to 4°, others are sometimes found which are not frozen by 24 hours' exposure to the temperature of a mixture of ice and salt. If well made, blasting gelatin exudes no nitroglycerin even after repeated freezing and thawing, but pressure tends to cause exudation, more so in some products than in others. Exudation ha frequently been traced to the use in manufactur of nitrocotton containing even small proportion of moisture. It usually shows first as a narrov line of free nitroglycerin along the edge of th inner fold of the wrapper. In the frozen state blasting gelatin is more sensitive to shock; rifle bullet can be fired through any numbe of unfrozen cartridges without exploding them but similarly fired through frozen cartridge never fails to cause their explosion. In th frozen state it is even more sensitive tha ordinary dynamite. For purposes of manipula tion, it is usually considered necessary to tha frozen cartridges before using them, and this i carried out in the same apparatus and with th same precautions as with kieselguhr dynamite The transmission of detonation through unfroze blasting gelatin is much slower than throug either nitroglycerin or dynamite, but the froze gelatin cartridges appear to detonate as quickl as those of dynamite. Blasting gelatin canno be exploded in trains in the open like dynamite but it explodes readily when confined in bore holes, and its comparatively slow detonatio makes it especially useful in blasting soft rock Between steel and steel, blasting gelatin explode under a blow of 25·3 foot-lbs. Soft blastin gelatin has been exploded between brass plate by a 56-lb. weight falling 12 feet, the heigh required when the blasting gelatin was froze being only 1 foot. From experiments made a Ardeer, it was found that while kieselguh dynamite No. 1 could be unfailingly explode by a detonator containing 0·05 gram of ca mixture (70 p.c. mercury fulminate and 3 p.c. potassium chlorate), the least quantity re quired to detonate the best blasting gelatin i 0·2 gram; and if the latter is tough, with a extra proportion of nitrocotton (*e.g.* with 9 p. or 10 p.c.), it fails to detonate completely eve with a 0·8 gram charge of cap compositio The velocity of detonation varies with the com position and physical condition. With a 20 grain detonator, Comey found that the velocit of detonation rapidly rose from about 2000 nea the point of detonation to about 6800 metre per second. Under poor confinement th detonating wave is subject to a steady fall o after reaching a maximum, and a sudden sto may occur if there is any break in the continuit of the explosive. Soft plastic products a more easily detonated than hard elastic ones. I is necessary, therefore, in order to get unfailin detonations with tough blasting gelatin, to us in actual mining a detonator with at leas 1 gram of cap composition, or to use a dynamit primer. Blasting gelatins which are of norm consistency when first manufactured, are liab to become hard and insensitive on storage. Th opinion usually held is that blasting gelatin h a webbed structure, and that the product i not sufficiently sensitive unless a considerab proportion of the nitroglycerin exists in th ungelatinised condition between the webs jelly. Hargreaves, who first propounded th theory, considers that blasting gelatin is be made by first forming a jelly with part of th nitroglycerin, and then adding the remaind without gelatinisation. He claims that th product manufactured in this way does n become insensitive on storage, and has b tendency to exude under warm storage conditions. The hardening and insensitiveness usually developed on storage, which appear to take place most readily at moderate temperatures, are attributed to the slow absorption of the free nitroglycerin by the collodion cotton. In small quantities, blasting gelatin burns away in the open without explosion. When gradually heated up, it explodes at about 204°; on rapid heating, it explodes at 240°. Blasting gelatin containing camphor cannot be exploded by gradual heating, but burns quickly away (Hess).

The addition of camphor (about 4 p.c.) to blasting gelatin deadens the sensitiveness of the latter to shock to a very remarkable extent. Rifle shots will not explode soft blasting gelatin containing 4 p.c. camphor at a distance of 150 paces. Berthelot attributes this effect to a certain amount of elasticity and solidity caused in the gelatin by the added camphor, on account of which the energy of the shock of the detonator, and the heat into which some of it is converted, are imparted to a much greater mass of substance than when no camphor is present—a condition unfavourable to a sudden and local rise of temperature. Before the introduction of 'ecrasite,' blasting gelatin containing 4 p.c. of camphor was used in Austria for military purposes as a high explosive. In Italy, 5 parts of camphor were added to 100 parts of nitrogelatin containing 8 p.c. of nitrocotton. These mixtures were so insensitive to shock that a special primer had to be used—in Austria, a mixture of nitroglycerin and nitrohydrocellulose; in Italy, guncotton. The French 'Dynamite-gomme, extra forte,' is a blasting gelatin containing 7–8 p.c. nitrocellulose.

Abel found (by the work done in expanding the bore of a lead cylinder) the intensity of action of Nobel's blasting gelatin to be about 160 when a sufficiently strong detonator was used, kieselguhr dynamite No. 1, exploded by the same detonator, being equal to 100. Abbot found the intensity of the same kind of blasting gelatin, detonated under water and referred to the same standard, to be 142. Hence it is not surprising that, although higher in price, blasting gelatin has to a large extent replaced kieselguhr dynamite.

According to Berthelot, the equation for the combustion of blasting gelatin containing 91·6 p.c. nitroglycerin and 8·4 p.c. nitrocellulose, the proportion for complete combustion is:

$$51C_3H_5(NO_3)_3+C_{24}H_{31}O_{11}(NO_3)_9 \\ =177CO_2+143H_2O+81N_2$$

The heat liberated by the equivalent weight, 12,360 grams, being 19,381 cals., or 1535 cals. per kilo.

Testing: *Heat test.*—50 grains of blasting gelatin intimately mixed with 100 grains of French chalk must withstand the Abel heat test at 160° for at least 10 minutes.

Liquefaction test.—A cylinder, of equal height and diameter, exposed to a temperature of 85° to 90°F. for 144 consecutive hours, must not diminish in height more than one-fourth of its original height, nor lose the sharpness of its edges.

Exudation test.—On subjecting, three times in succession, to alternate freezing and thawing, and in the liquefaction test, no substance of a less consistency than the bulk must separate out.

Although suitable in tunnelling for blasting hard rock and for military purposes, blasting gelatin is too local and violent in its effects for most mining operations, and various modifications were soon made to reduce its power. The usual way of doing this is to make a thinner gelatin and knead it into an absorbing powder. The earlier absorbents were usually a mixture of wood pulp or rye flour and either potassium or sodium nitrate. Many recent continental dynamites of this class contain ammonium nitrate, the explosives being then more powerful. The manufacture of these dynamites, which are also cheaper than blasting gelatin, is essentially the same as that of blasting gelatin.

Gelatin dynamite, made by Nobel's Explosives Company, consists of thin blasting gelatin mixed with wood meal and potassium nitrate. Its composition is: gelatinised nitroglycerin, 65 p.c.; potassium nitrate, 26·25 p.c.; 8·4 p.c. wood meal; 0·35 p.c. soda. The gelatinised nitroglycerin consists of 97·5 nitroglycerin and 2·5 p.c. soluble nitrocellulose. As usual, the proportions of the constituents vary in different samples: another gelatin dynamite containing nearly 80 p.c. gelatinised nitroglycerin, of about blasting gelatin composition, 16 p.c. nitre and 4 p.c. wood pulp. As made at Ardeer, the finished explosive is of pale buff colour and is very elastic. Abel, by the lead-cylinder method, found its intensity of action, when suitably detonated, to be 127 and 123 (mean 125), ordinary kieselguhr dynamite being 100.

The French 'Dynamite-Gomme,' 'Potasse,' and 'Soude' contain 82–83 p.c. nitroglycerin, 5–6 p.c. collodion cotton, 2–3 p.c. wood meal, and 9–10 p.c. potassium nitrate or sodium nitrate respectively.

The manufacture of dynamites of this class with wet collodion cotton was patented by Schachtebeck (Ger. Pat. 172651, 1905), the wet nitrocotton being treated with glue, dextrin, starch, or similar substance to absorb the moisture. An example given is 60 p.c. nitroglycerin, 7 p.c. collodion cotton containing 35 p.c. water, 3 p.c. glue, 7 p.c. wood meal, 20 p.c. sodium nitrate, and 3 p.c. ammonium nitrate. The Soc. Dynammit Akt. Ges. (Fr. Pat. 333443, 1903) suggests the use of carbohydrates soluble or partially soluble in water, such as sugar starch, dextrin, &c., in gelatin explosives, a plastic instead of a friable product with a low percentage of nitroglycerin being claimed. A composition given is 32 p.c. nitroglycerin, 0·7 p.c. collodion cotton, 18·5 p.c. dextrin, 1 p.c. vegetable oil, 35·8 p.c. ammonium nitrate, 3 p.c. ammonium oxalate, 2 p.c. wood meal, 2 p.c. sodium chloride, and 5 p.c. alum.

Gelignite is a weaker modification of gelatin dynamite, its composition being 60–61 p.c. nitroglycerin, 4–5 p.c. nitrocotton, 7–9 p.c. wood pulp, and about 27 p.c. potassium nitrate. This explosive is very largely used. It is frequently stabilised as in the case of blasting gelatin. An estimation by Abel of its intensity of action, suitably detonated in a lead cylinder, makes it 100, *i.e.* the same as the Ardeer kieselguhr dynamite No. 1.

The French '*Gélatines*' are of this class. A contains 64 p.c. nitroglycerin, 3 p.c. collodion cotton, 25 p.c. sodium nitrate, and 8 p.c. wood meal. *B-potasse*, or *-soudre*, contains about 57 p.c. nitroglycerin, 2·5–3 p.c. collodion cotton, 6–8 p.c. wood meal, and 32–34 p.c. potassium nitrate, or sodium nitrate, and *Gomme E* contains 49 p.c. nitroglycerin, 2 p.c. collodion cotton, 36 p.c. potassium nitrate, 10 p.c. wood meal, and 3 p.c. flour. French 'Gelignite' contains 58 p.c. nitroglycerin, 2 p.c. collodion cotton, 28 p.c. potassium nitrate, 9 p.c. wood meal, and 3 p.c. flour.

Ammonia gelatin A contains 30 p.c. nitroglycerin, 3 p.c. nitrocotton, and 67 p.c. ammonium nitrate.

Ammonia gelignite contains 29·3 p.c. nitroglycerin, 0·7 p.c. nitrocotton, and 70 p.c. ammonium nitrate.

Grisoutine Favier, a French safety explosive, contains 29·1 p.c. nitroglycerin, 0·9 p.c. collodion cotton, 69·5 p.c. ammonium nitrate, and 0 5 p.c. sodium carbonate.

Antigrison contains 27 p.c. nitroglycerin, 1 p.c. nitrocotton, and 72 p.c. ammonium nitrate.

Arkite No. 2, an English permitted explosive, contains on the average 32 p.c. nitroglycerin, 1 p.c. nitrocellulose, 27 p.c. potassium nitrate, 10 p.c. wood meal, and 30 p.c. ammonium oxalate. Limit charge 40 ozs., pendulum swing 2·41 inches.

Forcite. Although the early American forcites contained unnitrated cellulose, more recent samples, such as the Belgian, contain nitrocellulose, and are simply gelatin dynamites, containing from 40 to 65 p.c. of gelatinised nitroglycerin, 4–8 p.c. nitrocotton mixed with wood meal, rye flour or tar, and usually sodium nitrate, but in some cases ammonium nitrate or potassium nitrate; 1 p.c. magnesia and sulphur are also usually present. *Forcite antigrisouteuse* contains 29·4 p.c. nitroglycerin, 0·6 p.c. nitrocotton, and 70 p.c. ammonium nitrate.

Carbogelatin contains 38·5 p.c. of nitrogelatin, 49·5 p.c. nitre, 10·5 p.c. wood meal and charcoal, and 1·5 p.c. of magnesium carbonate.

Coronite contains 38–40 p.c. nitroglycerin, 1–1·5 p.c. nitrocotton, 26–28 p.c. ammonium nitrate, 3–5 p.c. potassium nitrate, 11 14 p.c. aluminium stearate, 8–11 p.c. rye flour, 2–4 p.c. wood meal, 2·4 p.c. liquid paraffin, and 0–2·5 p.c. moisture.

Duxite, on the English permitted list, contains, on the average, 32 p.c. nitroglycerin, 1 p.c. nitrocotton, 28 p.c. sodium nitrate, 10 p.c. wood meal, and 29 p.c. ammonium oxalate. Limit charge 12 ozs., pendulum swing 2·45 inches.

Two English explosives of this class on the permitted list, manufactured by Nobel's Explosives Company, are *Dynobel No.* 3, containing 14–16 p.c. nitroglycerin, 0·25–0·75 p.c. collodion cotton, 0·5–2·5 p.c. dinitrobenzene, di- and trinitrotoluene together, 51–54 p.c. ammonium nitrate, 4–6 p.c. wood meal, 24–26 p.c. sodium chloride, 0–1 p.c. magnesium carbonate, and 0–2 p.c. moisture. Limit charge 18 ozs., pendulum swing 2·50 inches; and *Dynobel No.* 4, a weaker variety, containing the same ingredients, but with less ammonium nitrate and more sodium chloride. Limit charge 30 ozs., pendulum swing 2·35 inches.

Essex powder, an English permitted explosive, contains 22–24 p.c. nitroglycerin, 0·5–1·5 p.c. collodion cotton, 33–35 p.c. potassium nitrate, 33–35 p.c. wheat flour, 5–7 p.c. ammonium chloride, and 2–5 p.c. moisture. Limit charge 38 ozs., pendulum swing 2·17 inches, detonator No. 6.

Gesilit is a modern German safety explosive. No. 1 contains 30·75 p.c. nitroglycerin jelly, 5·25 p.c. dinitrotoluene, 7 p.c. sodium chloride, 18 p.c. sodium nitrate, 39 p.c. dextrin. No. 2 contains 30·75 p.c. nitroglycerin jelly, 5·25 p.c. dinitrotoluene, 22 p.c. ammonium nitrate, 21 p.c. sodium chloride, and 21 p.c. dextrin.

Fordit, a similar explosive, contains 24 p.c. nitroglycerin, 1 p.c. nitrocotton, 34 p.c. nitrotoluene, 2 p.c. flour, 2 p.c. dextrin, 5 p.c. glycerin, and 32 p.c. ammonium nitrate; to this mixture is added 30 p.c. potassium chloride.

Celtite is a gelatin dynamite, with the addition of ammonium oxalate, having the composition 56–59 p.c. nitroglycerin, 2–3·5 p.c. nitrocotton, 17–21 p.c. potassium nitrate, 8–9 p.c. wood meal, 11–13 p.c. ammonium oxalate, and 0·5–1·5 p.c. moisture.

Geloxite is a similar explosive which contains 54–64 p.c. nitroglycerin, 4–5 p.c. nitrocotton, 13–22 p.c. potassium nitrate, 4–7 p.c. wood meal, containing not more than 15 p.c. and not less than 5 p.c. moisture, 12–15 p.c. ammonium oxalate, and 1 p.c. red ochre. Ochre is sometimes added to dynamites to make them resemble ordinary dynamites in appearance.

Haylite No. 1, an English permitted explosive, contains 25–27 p.c. nitroglycerin, 0·5–1·5 p.c. collodion cotton, 19–21 p.c. potassium nitrate, 19–21 p.c. barium nitrate, 12–14 p.c. wood meal, 6–8 p.c. mineral jelly, 10–12 p.e. ammonium oxalate, and 0·5–2·5 p.c. moisture. Limit charge 10 ozs., pendulum swing 2·18 inches, detonator No. 6.

Ripplte, an English authorised explosive, contains 56–63 p.c. nitroglycerin, gelatinised with a small quantity of collodion cotton, potassium nitrate, wood meal, castor oil, and ammonium oxalate, and is stabilised by the addition of a little calcium or magnesium carbonate, or mineral jelly.

Saxonite, manufactured by Nobel's Explosives Company, was at one time on the permitted list, and the most extensively used of safety explosives in this country. It contains 42·5–62 p.c. nitroglycerin, 2·5–5 p.c. collodion cotton, 16–27·5 p.c. potassium nitrate, 3·5–8 p.c. wood meal, 9–27 p.c. ammonium oxalate, and 0–0 5 p.c. calcium carbonate. It failed to pass the Rotherham test, but is still used for purposes other than in fiery mines.

Samsonite, an explosive of closer limits, was designed by Nobel's to replace 'Saxonite,' and is at present on the permitted list. Its composition is: 57–60 p.c. nitroglycerin, 3–4 p.c. collodion cotton, 17–19 p.c. potassium nitrate, 5–7 p.c. wood meal, 12·5–14·5 p.c. ammonium oxalate, and 0–1·5 p.c. moisture.

Stowite contains 58–61 p.c. nitroglycerin, 4·5–5 p.c. nitrocotton, 18–20 p.c. potassium nitrate, 6–7 p.c. wood meal specified as in geloxite, and 11–15 p.c. ammonium oxalate. A non-waterproofed wrapper of parchment is used, and a No. 6 detonator.

Syndite is on the English permitted list. It contains 10–22 p.c. nitroglycerin, 0·1–0·3 p.c.

collodion cotton, 45–49 p.c. ammonium nitrate, 7–9 p.c. sodium nitrate, 2–5 p.c. glycerin, 2–5 p.c. starch, 26–28 p.c. sodium chloride, and 0–2 p.c. moisture. Limit charge 40 ozs., pendulum swing 2·22 inches, detonator No. 7.

Super-Cliffite is manufactured by Curtis's and Harvey in two varieties. *No.* 1 contains 10 p.c. nitroglycerin, less than 1 p.c. collodion cotton, 60 p.c. ammonium nitrate, 16 p.c. sodium chloride, 11 p.c. ammonium oxalate, 6 p.c. wood meal, and 2 p.c. moisture; limit charge 26 ozs., pendulum swing 2·53 ins.; and *No.* 2 of similar composition, except that the sodium chloride is increased to 20 p.c. and the ammonium oxalate reduced to 6 p.c.; limit charge 30 ozs., pendulum swing 2·53 ins.

The permitted composition for *Phœnix powder* is 28–31 p.c. nitroglycerin, 0–1 p.c. nitrocotton, 30–34 p.c. potassium nitrate, 33–37 p.c. wood meal, and 2·6 p.c. moisture.

Safety dynamite contains 24 p.c. nitroglycerin, 1 p.c. nitrocotton, and 75 p.c. ammonium nitrate.

The *wood pulp*, so frequently used as an ingredient in these dynamites, is made from logs usually of pine wood, but occasionally from other woods. The logs are freed from bark and sawn into boards; the boards, free from knots, broken by a machine into small pieces and then crushed between rollers. Where available in sufficient quantity, shavings are used. The powder is boiled under pressure with a solution of sodium bisulphite for 10 to 12 hours. The pulp is then washed and dried. The pulp must not be exposed to acid vapours or overheated in drying, and should all pass through a sieve of 50 meshes to the inch. It should not be too fine, or the resulting dynamites are too dense in character and difficult to detonate.

The use of non-fermentable *starch* was proposed by Kynoch (Eng. Pat. 22966, 1901) as a substitute for wood meal, in order to reduce the bulk of the explosive.

Cocoanut fibre has been suggested by Gonsalves (Eng. Pat. 4968, 1905) as an absorbent for this class of dynamite, and it is claimed that it prevents the freezing of the nitroglycerin.

Guncotton dynamite. In 1867 mixtures of nitroglycerin with pulped guncotton, which, unlike collodion cotton, does not dissolve in and gelatinise nitroglycerin, were proposed by Abel and Trauzl. Abel's mixture was called *glyoxiline*, and was prepared by soaking guncotton, with or without nitre, in nitroglycerin.

Trauzl's dynamite consisted of 75 p.c. nitroglycerin, 25 p.c. guncotton, and 2 pts. charcoal to every 100 of mixture. In 1868 Schultze proposed a mixture of nitrated wood cellulose soaked in nitroglycerin under the name of '*dualine.*'

These explosives, like most other dynamites, have been superseded by the gelatin dynamite class.

Freezing of dynamites.—The comparatively high freezing-point of nitroglycerin, and the difficulty in thawing, is a great objection to the use of nitroglycerin explosives. Numerous attempts have been made to overcome the difficulty by lowering the freezing-point, by suitable additions, but with very limited success. In England it is usual to take precautions to prevent freezing by suitable storage in warm magazines, but in the United States and on the Continent additions to the nitroglycerin to prevent freezing are common. The addition of nitrohydrocarbons such as nitrobenzene was tried by Nobel and Guttmann, but they found that so large a quantity was required to produce any sensible reduction of the freezing-point, that the power and sensitiveness of the explosive were seriously reduced. This reduction of power is of advantage in safety explosives, and nitrohydrocarbons in small amount are frequently constituents in dynamites of this class. The lower the molecular weight of the nitro body the smaller the percentage necessary to effect a given reduction of freezing-point, but the nitrohydrocarbons of low molecular weight have the disadvantage of being volatile. The addition of nitrobenzene had been previously patented in Sweden by Rudberg in 1860, and von Dahmen in Austria patented a process for nitrating glycerin mixed with a small percentage of nitrobenzene. Dinitrotoluene was found more efficient, and its use was patented by the Société des Poudres, &c. Dynamites, of Arendonck in 1903 (Eng. Pat. 14827, 1903) and a mixture of solid di- and trinitrotoluene was suggested by Johnson (Eng. Pat. 25797, 1904). In the United States low-freezing dynamites, such as the Red Cross Dynamites of the E. I. du Pont de Nemours Company, are manufactured by replacing about one-fourth of the nitroglycerin of the 'straight dynamites' by a nitrohydrocarbon.

Wohl, in 1890, had suggested the use of mono- and dinitroglycerin for reducing the freezing-point of nitroglycerin, and in 1904 Mikolajczak patented the use of dinitroglycerin (Eng. Pat. 8041, 1904); but mono- and dinitroglycerin are hygroscopic, soluble in water, and expensive, and moreover Will has shown that their addition is not very effective.

The Westfälisch-Anhaltische Sprengstoff-Gesellschaft, in 1906, patented the use of nitrochlorhydrins and subsequently the nitropolyglycerins (Eng. Pat. 4057 and 6314, 1906). Dinitrochlorhydrin is now used to a large extent in German nitroglycerin explosives, such as 'Gelatin Astralit,' 'Gelatin Donarit,' and 'Gelatin Westfalit,' for this purpose. It is easy and cheap to manufacture, and mixes with nitroglycerin in all proportions, and gelatinises collodion cotton equally well. Its admixture up to 20 p.c. of the nitroglycerin has very little effect on the explosive properties of the dynamites. The mixture is made by nitrating a mixture of glycerin and chlorhydrin in the usual way. Dinitrochlorhydrin is practically insoluble in water, and is not hygroscopic, but it has the disadvantage that it gives off hydrochloric acid on explosion, and necessitates the use of an alkaline nitrate in dynamites containing it, if for use underground. Vender proposed dinitroacetin and dinitroformin (Eng. Pat. 9791, 1906), which have the advantage that hydrochloric acid is not one of the products of explosion, and Escales (Eng. Pat. 2117, 1907) used a nitrated complex mixture of mono- and di-chlorhydrin, di- and tri-glycerin and the chlorhydrins of these bodies.

The subject of the lowering of the freezing-point of nitroglycerin has been investigated by

Nauckhoff (Zeitsch. angew. Chem. 1905, 11, 53). He showed that the freezing-point of a nitroglycerin explosive can be calculated from its composition, by means of Raoult's formula, and that the value of a substance for depressing the freezing-point of nitroglycerin depended on its molecular weight and not on its own freezing-point. He pointed out, further, that the resistance to freezing depended, not only on the true freezing-point of the mixture, but also on its property of undergoing cooling below its freezing-point without solidifying, and found that the property was best shown in more plastic explosives.

NITROCELLULOSES.

Braconnot, in 1832, observed that starch, woody fibre, and other similar substances, are converted by the action of strong nitric acid into a combustible product, which he called *xyloïdine*. Pelouze, in 1838, found that starch treated with strong nitric acid increased in weight; and that paper, cotton, and linen, immersed in nitric acid of 1·5 sp.gr., become easily combustible. Schönbein, towards the end of 1845, announced the discovery of a new explosive substance, which he subsequently stated to have been obtained by treating cotton with a mixture of nitric and sulphuric acids. Böttger, in August, 1846, found out the method of making guncotton, which Schönbein was keeping secret. The two chemists jointly submitted their discovery to the Germanic Confederation, but reserved the publication of their method of preparing guncotton. Several chemists having in 1847 independently discovered the method of preparing guncotton by means of a mixture of nitric and sulphuric acids, Schönbein and Böttger then stated this to be their process. The manufacture of guncotton was undertaken in England, France, and Russia; but the earlier attempts at manufacture were not satisfactory, the importance of purifying the cotton from fatty matter, and of washing the guncotton thoroughly free from acid, not having at first been sufficiently felt to be essential to obtaining a safe and stable guncotton.

Von Lenk, in Austria, between 1849 and 1852, made great improvements in the manufacture of guncotton; and in 1853 a factory was erected under his direction at Hirtenberg, near Vienna, in which (and at Reny in Vienna) the manufacture was continued until 1865, when the manufacture and use of guncotton were officially put a stop to in consequence of the explosion of two magazines. Von Lenk used the cotton in the form of yarn; his principal improvements were the purification of the cotton from oily and other matters by boiling with caustic alkali, the nitration of the cotton in separate small charges, the dividing the operation of nitration into two stages: a short immersion (of some minutes) of the cotton in the mixed acids, the removal of the cotton with a sufficiency of absorbed acids, and allowing a long time (24 to 48 hours) for the completion of the nitration, also the careful washing of the guncotton to remove free acid. To remove acid, the guncotton after its nitration was whirled in a centrifugal machine, washed in copper drums with a large quantity of water, then placed in boxes in running water for three to six weeks, after which it was treated with a hot weak solution of potash, and again water-washed.

Von Lenk's guncotton was used in the form of yarn.

Abel, adopting Von Lenk's method of nitrating the cotton, made very important improvements in the processes of manufacture. He introduced the use of cleaned cotton waste, and by converting the guncotton into pulp so facilitated the washing that it could be effected in two or three days instead of in six or more weeks as in Von Lenk's process. Further, by compressing the finished pulp by hydraulic pressure, he rendered it possible to detonate it in an unconfined state. The pulping and compressing of the guncotton were introduced in 1865 (Eng. Pat. 1102, 1865).

Composition.—Guncotton, when the process of manufacture has been well conducted, and when the strongest acids have been used, has the composition of trinitrocellulose $C_6H_7O_2(NO_3)_3$, when cellulose is $C_6H_{10}O_5$.

This composition was deduced by Abel from the results of a large number of analyses (in which C, H, and N were determined) of guncotton of Waltham Abbey make. The mean numbers given by these analyses of the dry guncotton, ash deducted, are given below, and are compared with the percentages calculated for trinitrocellulose:

	Mean of analyses	$C_6H_7O_2(NO_3)_3$
Carbon . .	24·57	24·24
Hydrogen . .	2·46	2·36
Nitrogen . .	13·83	14·14
Oxygen . .	59·14	59·26

The percentage of carbon is slightly raised, and that of nitrogen slightly depressed, by the presence in the guncotton of a few per cents. of less highly nitrated cellulose than the trinitro derivative, and soluble in ether alcohol (Abel, Phil. Trans. 1866, 156, 269–308).

The formation of trinitrocellulose from cellulose is represented by the equation:

$$C_6H_{10}O_5+3HNO_3=C_6H_7O_2(NO_3)_3+3H_2O$$

from which 100 parts by weight of cotton should give 183·3 parts by weight of trinitrocotton.

Abel (*l.c.*), as the result of a large number of experiments, found a maximum increase of 82·6 p.c., which is a close approach to the theoretical 83·3 p.c., and confirms Hadow's previously observed increase of 81·3 p.c.

Soluble nitrocellulose.—Abel found that the part of guncotton soluble in a mixture of alcohol and ether is a less highly nitrated compound than his trinitrocellulose; it approaches in composition dinitrocellulose (Proc. Roy. Soc. 1866). In a further series of experiments, in 1868, Abel examined the influence on the nitration of the cotton of an addition of water to the acids. Using mixtures of 60 lbs. nitric acid, sp.gr. 1·42, and 65½ lbs. sulphuric acid, sp.gr. 1·838, without addition of water, and also with the addition of 3 lbs. of water, he obtained nitrocottons, which, after reprecipitation from solution in ether-alcohol, had percentages of carbon 28·56 and 28·13 respectively: the calculated percentage in dinitrocellulose $C_6H_8O_3(NO_3)_2$ being 28·57.

For a long time, nitrocelluloses were divided into two kinds only—trinitrocellulose, guncotton, or insoluble nitrocellulose, and dinitrocellulose, collodion cotton, or soluble nitrocellulose; but it was clearly shown in the cordite case, Nobel v. Anderson, 1894, that there are certainly more than two cellulose nitrates, and, further, that the solubility of the nitrocellulose is not invariably related to the degree of nitration, but that soluble nitrocellulose can be prepared containing almost as much nitrogen as guncotton.

Roscoe prepared, for example, a soluble nitrocellulose containing 12·73 p.c. of nitrogen, and an insoluble nitrocellulose with 12·83 p.c. of nitrocellulose.

Eder, as he was able to prepare nitrocottons in which the percentage of nitrogen is between those corresponding to the above tri- and dinitrocellulose, doubled Abel's formulæ, and claimed to have prepared the following five varieties of nitrocellulose:—

			P.c. of nitrogen
$C_{12}H_{14}O_4(NO_3)_6$ Hexa-nitrocellulose,	containing		14·14
$C_{12}H_{15}O_5(NO_3)_5$ Penta-	„	„	12·75
$C_{12}H_{16}O_6(NO_3)_4$ Tetra-	„	„	11·11
$C_{12}H_{17}O_7(NO_3)_3$ Tri-	„	„	9·15
$C_{12}H_{18}O_8(NO_3)_2$ Di-	„	„	6·76

His hexanitrocellulose only was insoluble in ether-alcohol, and is ordinary guncotton.

Vieille (Compt. rend. 1882, 132) prepared nitrocottons under the most varying conditions, and stated that the nitration of cellulose, which he assumed to be $C_{24}H_{40}O_{20}$, took place in eight stages, the products being:

			P.c. of nitrogen
$C_{24}H_{29}O_9(NO_3)_{11}$ Endeca-nitrocellulose,	containing		13·50
$C_{24}H_{30}O_{10}(NO_3)_{10}$ Deca-	„	„	12·78
$C_{24}H_{31}O_{11}(NO_3)_9$ Ennea-	„	„	11·98
$C_{24}H_{32}O_{12}(NO_3)_8$ Octo-	„	„	11·13
$C_{24}H_{33}O_{13}(NO_3)_7$ Hepta-	„	„	10·19
$C_{24}H_{34}O_{14}(NO_3)_6$ Hexa-	„	„	9·17
$C_{24}H_{35}O_{15}(NO_3)_5$ Penta-	„	„	8·04
$C_{24}H_{36}O_{16}(NO_3)_4$ Tetra-	„	„	6·77

Of these, the endeca- and deca-nitrocelluloses were insoluble in ether-alcohol.

Berthelot, following Vieille, regards guncotton as $C_{24}H_{29}(NO_2)_{11}O_{20}$ (mol. wt. 1143).

He finds the heat evolved by the nitration of cotton in accordance with the equation:

$$C_{24}H_{40}O_{20}+11HNO_3=C_{24}H_{29}O_9(NO_3)_{11}+11H_2O$$

to be 11 × 11·4=125·4 kgm.-degrees per 1·143 kgm. of guncotton formed. The heat of formation of endecanitrocellulose from its elements (diamond carbon, gaseous hydrogen, oxygen, and nitrogen), Berthelot finds to be +624 kgm.-degrees per 1·143 kgm., or +546 kgm.-degrees per 1 kgm.

These formulæ of Vieille were soon contested. Guttmann claimed to have made guncotton on the large scale containing 13·65 p.c. nitrogen; Hoitsema (Zeitsch. angew. Chem. 1898, 173) obtained a product containing 13·9 p.c. nitrogen; and Lunge (J. Amer. Chem. Soc. 1901, 527), with an acid mixture containing 63·35 p.c. H_2SO_4, 25·31 p.c. HNO_3, and 11·34 p.c. water, prepared nitrocellulose with 13·92 p.c. nitrogen, corresponding very closely to

$$C_{24}H_{28}O_8(NO_3)_{12}$$

dodecanitrocellulose, containing 14·16 p.c. nitrogen; but this substance, like that with a similar nitrogen content, obtained by nitrating cotton with a mixture of equal parts of nitrogen pentoxide and phosphorus pentoxide (*cp.* Holtsema, *l.c.*), was not stable, and on keeping, the nitrogen content fell to 13·5 p.c., at which point it remained constant. In a further series of experiments, Lunge found that when all water was eliminated by adding fuming sulphuric acid, the p.c. of nitrogen was not altered, even when such varying ratios of H_2SO_4 to HNO_3 as 3·3 : 1 to 2 : 1 were used. Tassart (Bull. Soc. chim. 1912, 1009), by the successive action of cold sulphuric and nitric acids on cotton, has prepared a product which he terms *α-nitrocellulose*, containing 13·5 p.c. nitrogen. It is white, easily powdered, insoluble in water, but soluble in methyl and ethyl alcohols, and very unstable.

Lunge found that with nitrocellulose of less than 10 p.c. nitrogen, the solubility rapidly decreased and confirmed Vieille's results that below $C_{24}H_{32}O_{14}(NO_3)_6$ the products are insoluble. He also found that with dilute acids the products contained oxycellulose, the proportion of the latter gradually increasing unti eventually it was the only product. Saposchnikoff (Zeitsch. ges. Scheiss- u. Sprengstoffwesen, 1906, 453) shows a close relationshi between the vapour pressure of the nitric acic in the mixed acids and the nitrogen content o the products.

Berl and Klaye (Zeitsch. ges. Schiess- u Sprengstoffwesen, 1907, 403) show that th process of nitration of cellulose is a reversibl reaction, represented by the equation:

$$C_{24}H_{40}O_{20}+nHNO_3 \rightleftarrows C_{24}H_{40-n}O_{20-n}(NO_3)_n+nH_2C$$

and that after a certain maximum substitutior is obtained, about 13·5 p.c. nitrogen, the sulphuric acid of the nitrating mixture acts as hydrolysing agent.

Berl and Smith (Ber. 1907, 1903) prepare esters of cellulose in order to show the numbe of free hydroxyl- groups in the cellulose molecule They found it impossible to introduce more tha twelve substituted groups into the cellulos molecule of $C_{24}H_{40}O_{20}$, which agrees with th results of Ost (Zeitsch. angew. Chem. 1906, 993) and Green and Perkin (Chem. Soc. Trans. 1906 811), but did not succeed in obtaining a nitro cellulose with a higher nitrogen content tha 13·50 p.c.

Any preparation of nitrocellulose is a mixture of definite nitrates, the nature of whic depends on the nature of the nitrating mixtur the time and temperature of nitration, and th method of purification. Vieille (Compt. rend 1882, 132) prepared nitrocellulose containin up to 12·7 p.c. nitrogen by the use of nitric aci alone in large excess, but the nitration is slow and difficult, and it is the invariable custom t use a mixture of nitric and sulphuric acids. E is probable that the cellulose first reacts with the sulphuric acid, and that the product in turn reacts with the nitric acid to form nitrocellulose. When much water or sulphuric acid is present the process is slow and the nitration low. A higher degree of nitration is obtained by raising the temperature, but this can only be done within limits, or oxycellulose and nitrooxycellulose are formed, and part of the cellulose is completely broken down at high temperatures. The effect of a high proportion of water in breaking down the cotton is particularly noticeable.

A large excess of mixed acids is necessary in the nitration of cellulose, partly because of the bulk of the latter, but also to obtain products of constant composition. The acid mixture is diluted during nitration, both by the formation of water and by the abstraction of nitric acid during the nitration, and both these factors tend to lower the nitrogen content of the product, unless the bulk of the mixed acids is large. The speed of nitration is diminished with increase in the quantity of sulphuric acid.

As far as explosives are concerned, only two forms of nitrocellulose need be distinguished: guncotton or insoluble nitrocotton, and collodion or soluble nitrocotton. The explosive power of the nitrocellulose is dependent on the degree of nitration, and each variety is prepared of definite nitrogen content according to its use. When the soluble nitrocellulose is referred to in this article without qualification, solubility in ether-alcohol is always inferred.

Nitrohydrocellulose and *nitrooxycellulose.* Hydrocellulose $C_{12}H_{22}O_{11}$, cellulose being $C_{12}H_{20}O_{10}$, is prepared by soaking cotton for 12 hours in sulphuric acid of 1·45 sp.gr. at 15°, or for 24 hours in hydrochloric acid of 1·17 sp.gr. (Girard). Cross and Bevan prepared oxycellulose by boiling cellulose with nitric acid, and found its composition to be $C_{18}H_{26}O_{16}$. The nitro body obtained from it by nitration with a mixture of equal volumes of strong sulphuric and nitric acids, contained 6·48 p.c. nitrogen, and was given the formula:

$$C_{18}H_{23}O_{13}(NO_3)_3$$

(Chem. Soc. Trans. 1883, 22).

Vignon (Compt. rend. 1898, 136) found that oxycellulose, prepared by the action of a mixture of hydrochloric acid and potassium chlorate on cellulose, had a constant composition represented by $3C_6H_{10}O_5+C_6H_{10}O_6=C_{24}H_{40}O_{21}$.

Both these bodies, which may be formed in the nitration of cellulose, can be themselves nitrated. Hydrocellulose nitrates more slowly than cellulose, giving stable but rather sensitive products, and oxycellulose gives an unstable nitro product. Amorphous nitro products of oxy- and hydro-cellulose can be prepared by treating cellulose with sulphuric acid containing a little nitric acid at a low temperature until the mass becomes pasty, then nitrating and purifying as usual. Crane and Joyce (J. Soc. Chem. Ind. 1910, 540), by nitrating cotton with an acid mixture containing 9·0 p.c. HNO_3, 65·5 p.c. H_2SO_4, and 25·5 p.c. H_2O, obtained a nitrohydrocellulose of the composition

$$C_{24}H_{28}O_{20}NO_2\cdot 2H_2O$$

which was insoluble in acetone and ether-alcohol, but soluble in strong acids and caustic alkali. Vignon (*l.c.*) found that nitrocellulose, prepared according to Lunge's formula for highest nitration, gave on determination of their C, H, and N, results agreeing with the formula

$$3C_6H_7O_2(NO_3)_3+C_6H_7O_3(NO_3)_3 =C_{24}H_{28}O_9(NO_3)_{12}$$

He concludes from this that this so-called nitrocellulose is an oxycellulose derivative, and attributes discrepancies in the results of others to the fact that the nitrogen only is estimated.

Later (Compt. rend. 1900, 509), Vignon determined the copper-reducing powers of nitrated cellulose and nitrooxycellulose, and found them identical and independent of the degree of nitration, and as oxycellulose reduces cupric potash solution, whilst cellulose and hydrocellulose do not, concludes that, on the nitration of cellulose, oxycellulose is formed, and that the product is really nitroxycellulose.

Guncotton.

Manufacture.—The only process of manufacture of guncotton, with some modification in detail, was for some years the process of Von Lenk, as modified and improved by Abel. Other processes, notably the 'Thomson displacement process,' introduced at Waltham Abbey in 1905, and the 'nitrating centrifugal process,' are now more generally used.

Prime materials: *Cellulose.*—Although many forms of fibrous cellulose materials have been from time to time tried, practically the only form of cellulose in general use for the manufacture of guncotton is the cotton waste from spinning mills and other sources. New cotton would be the best raw material for use, but it is too expensive. 'Cop-bottoms,' the last portion of cotton left on the spindles, and usually in a tangled condition, are frequently used for the manufacture of collodion cotton, but this again is too expensive for general use. 'Linters,' the last portion of cotton from the seed, is largely used in the United States and on the Continent for the manufacture of soluble nitrocotton, but the drastic treatment necessary for the removal of the adherent seed-husk and resinous matter, and the fermentative changes that take place in the cotton if left in contact with the husk, adversely affect the quality of the guncotton manufactured from 'linters.' 'Weaving mill waste' is contaminated with starch, as this is applied to the warps to strengthen them, and can only be used for the manufacture of nitrocotton after the starch has been suitably removed, as the nitration products of starch are unstable. The quality of the waste from different sources varies considerably, and it is important that it should be as pure as possible in order to obtain a good yield of pure guncotton. The previous treatment of the cellulose has been shown by Piest (Zeitsch. angew. Chem. 1909, 215) to have considerable influence on the preparation and properties of nitrocellulose. The product from strongly bleached or mercerised cotton has a lower nitrogen content and higher solubility, and is more difficult to stabilise than that from ordinary cotton. Hake and Bell (J. Soc. Chem. Ind. 1909, 460) showed that the physical condition of the cellulose affects the nitration. If the cotton is dense the nitration is slow, and a larger proportion of the sulphuric ser is formed with resultant loss in yield. nge showed that the source of the cotton has ttle effect on the product. The viscosities of lutions of cotton have been investigated by st (Zeitsch. angew. Chem. 1911, 1892) and thers with a view to determining the suitability f the cottons for nitration, and to establishing relationship with the stability of the nitroroducts. Solutions in cuprammonium are sed. New cotton gives more viscous solutions han cotton waste, especially when this has been hemically treated and bleached, no doubt wing to a greater molecular complexity, and he nitrocottons prepared from them give soluions in acetone differing in viscosity in the same direction. Piest (Zeitsch. angew. Chem. 1913, 26, &c.) showed that nitrocellulose solutions become less viscous on standing to an increasing extent the more the cellulose has been bleached. This he attributes to the presence of impurities, such as the esters of oxycellulose.

Formerly the waste was purified by boiling with a 2 p.c. solution of sodium carbonate and subsequent washing, but the modern purification process is more complicated. The waste is first of all de-greased by means of a solvent, then boiled in a kier with a weak solution of sodium carbonate or caustic soda, bleached with bleaching powder or calcium sulphide, washed, neutralised with sulphuric or hydrochloric acid, washed again, and finally dried. In detail, the process of purification varies with the type of waste being treated. Levine (J. Ind. Eng. Chem. 1916, 298) suggests the removal of impurities by bacterial treatment. The resultant cotton is nearly pure cellulose, with little or no altered, oxy-, or hydro-cellulose. It should contain no chloride, sulphate, or sulphide of lime, and be free from starch, and from cotton dust, or 'fly.' It contains less than 0·3 p.c. of fatty matter, but usually the uncarded waste used in the manufacture of guncotton contains a considerable quantity of impurities, such as wood, cane, string, coloured threads, metal, indiarubber, &c. These impurities and any hard knots of cotton are removed as far as possible by handpicking, and the cotton is then passed through a 'teasing machine' or 'willow,' a combination of drums armed with sharp-pointed teeth, which tear the threads apart and open out the knots and lumps. The cotton is picked over again as it leaves the machine, dried until the moisture content is about 0·5 p.c. on an endless band in a current of hot air, which is often first dried over sulphuric acid or calcium chloride, and then weighed out in charges, placed in tightly closed receptacles, and allowed to cool.

Mixed acids.—The acids used in the manufacture of guncotton are of a high degree of purity, free from solids, and of maximum concentration. The proportions of acid employed until recently were those used by Von Lenk, namely, 1 part of nitric acid of 1·5 sp.gr., containing not more than 1·5 p.c. of nitrous acid, and 3 parts of sulphuric acid of 1·84–1·85 sp.gr. In other words, the nitric acid contained at least 93 p.c. of monohydrate, and the sulphuric acid 95–96 p.c. of monohydrate. The more modern mixtures vary slightly in composition according to the method of nitration, and are given under these various methods.

The experiments of Lunge (*l.c.*) have shown that it is not necessary to have acid mixtures containing only a few per cents. of water, and that with acids of the proportion of $3H_2SO_4$ to $1HNO_3$, it is possible to work with as much as 12 p.c. of water. Not only is the acid mixture cheaper, but Lunge agrees with Will that the nitrocellulose manufactured with the more dilute mixtures is more stable than when produced by highly concentrated acids. Lunge also investigated the influence of nitrous acid on the quality of the product, and found that with contents of nitrous acid up to 6 p.c. of the mixed acid there was practically no influence on the nitrogen content, the solubility or stability of the product, but there is some doubt as to whether the stability of the product is not adversely affected to a slight extent when the proportion of nitrous acid is unduly high.

Most explosive factories have plant for the manufacture of the nitric acid, and for the recovery of waste acids, the latter being revivified and used again. The acids are mixed in large quantities, analysed, and the composition adjusted to that required, by the addition of strong acids in the requisite proportions. Nordhausen sulphuric acid or 'oleum' is now in common use for decreasing the proportion of water.

Mechanical mixing of the acids was at one time generally practised, but it was subsequently found that a perfect admixture was obtained by running the sulphuric into the nitric acid. However, the acids are now frequently mixed by means of compressed air, means being adopted to condense the nitric acid vapours.

The acids are stored and transferred from place to place as already described in the manufacture of nitroglycerin.

Nitration.—Lunge (*l.c.*) has shown that the speed of nitration increases rapidly, but the yield falls, owing to solution of the product in the mixed acids, with rise in temperature, the nitrogen content of the product varying but slightly. He concludes that the ordinary method of nitrating at a temperature not exceeding 25° is correct for obtaining maximum nitration and maximum yield. An outline of the nitration process used by Von Lenk has already been given.

Abel's nitration process, as formerly carried out at the Royal Gunpowder Factory, Waltham Abbey, and still used in many factories in England and abroad, is shortly as follows :—

The mixed acids are drawn off from the store tanks into a tank in connection with the dipping pans. These latter are of cast iron, arranged in a tank through which cold water is circulated to keep the temperature during the nitration below 22° ; each holds about 220 lbs. of mixed acids, and is provided with a grating. The charge of 1¼ lb. of cotton is then, by small portions, quickly immersed in the mixed acids, which at Waltham Abbey was composed of 3 parts of sulphuric acid, 96 p.c., and 1 part of nitric acid, 91 p.c., mixed and thoroughly cooled. After an immersion of 5 or 6 minutes, the cotton is removed to the grating, and squeezed by means of a lever with a plate at one end. The charge, which with the acid now weighs about [illegible]6 lbs., is placed in a closely covered earthen pot, in which it is allowed to remain for from 12 to 24 hours, during which time the pots are placed in constantly flowing cold water. By this prolonged action, the nitration of the cotton is completed; the cooling is needed to prevent complete decomposition of the product by oxidation, and the maintenance of a low temperature is said to be favourable to the production of guncotton with a low percentage of soluble nitrocotton.

Much of the acids is then removed from the guncotton by means of the centrifugal machine made entirely of iron, the contents of six pots being whirled for 10 minutes at the rate of about 1200 revolutions per minute. The guncotton is then, carried in small quantities in galvanised iron pans, emptied out and plunged by means of an iron fork or wooden paddle beneath a cascade of water, which carries it into a large cistern, where it is kept stirred by a paddle wheel, and is washed by fresh water continually admitted, until the guncotton has no perceptible acid taste, when it is whirled in a centrifugal machine, with a short washing with water at the end of the whirling, after which it is ready for the boiling process. The immersion in the water has to be carried out quickly, as the acid guncotton is liable to 'fume off' on slow contact with water. The yield by this process is about 164 p.c. of the cotton nitrated.

In the Abel process, there is considerable wear and tear of the plant, and there is occasionally loss of guncotton owing to decomposition or 'fuming off' taking place in the digesting pots. Moreover, there is a considerable expenditure of labour and power involved, and improvements have been made to overcome these disadvantages.

Direct-dipping process.—In the direct-dipping process, as used at Nobel's factory at Ardeer, the operation of nitration is completed in one stage. The nitration is carried out in a series of iron pots, termed 'dippers,' standing in cold water contained in long cooling tanks, the pots being closed by covers which lead away the acid fumes to exhaust pipes. Each dipper is fed with 127 lbs. of mixed acid, the temperature of the acid is adjusted to 15°, and the charge of 4½ lbs. of cotton gradually added, the temperature rising to 25°. The nitration is allowed to proceed for from 8 to 24 hours, according to the composition of the nitrating mixture, the temperature gradually falling to 20°. The mixed acid for a 12 hours' immersion is 75 p.c. sulphuric acid, 15·75 p.c. nitric acid (monohydrate) and 9·25 p.c. water. The more rapid the nitration, the higher the proportion of nitric acid and the less the proportion of water used.

When the nitration is complete, the contents of the dippers are transferred to centrifugals, and the waste acids whirled out. The guncotton is then treated as in the Abel process. The yield by this process is about 159 p.c. of the cotton nitrated.

Centrifugal process.—In this process, largely used on the Continent, the nitration is carried on in a perforated iron basket, rotating in an outer iron casing, the centrifugal being jacketed for temperature control by water circulation and covered with a lid fitted with a fume pipe. The nitrating acid is run in and the cotton charge of 17¼ lbs., or in a large sized centrifugal 66¼ lbs., gradually added whilst the basket is slowly rotating. The effect of the rotation is to produce better contact between the cotton and acids, and the nitration only occupies from 30 minutes to an hour. When the nitration is complete, the bulk of the waste acid is drawn off, and the centrifugal set rotating rapidly, the guncotton being afterwards 'pre-washed' as usual. It is necessary not to reduce the acid content too far in the wringing, otherwise the charge is liable to 'fume off.' The nitrated charge is removed by tongs to an automatic conveyor, which transfers it at once to the drowning tank.

In this process the nitrating acid is about fifty times the weight of the cotton charge, the composition of the acid being about 23·15 p.c. HNO_3, 69·35 p.c. H_2SO_4, and 7·5 p.c. water. As this process is more rapid than the 'Abel process,' and since the velocity of nitration is decreased by a high content of sulphuric acid, it is necessary that the proportion of nitric acid in the mixed acid should be higher.

The usual forms of nitrating centrifugal used are those of Messrs. Selwig and Lange, of Brunswick, who, in 1904, patented an improved form in which the acid is caused to circulate continuously through the material by means of a pump, for the purpose of producing a more uniform nitration and avoiding local centres of heating.

Guttmann suggested the use of aluminium baskets, but, although more acid-resisting than the usual cast-iron baskets, the metal was found to be too soft and to get out of shape. The yield by this process of nitration is 160 p.c. of the cotton nitrated.

Displacement process.—In 1903 (Eng. Pat. 8278) J. M. and W. T. Thomson, of the Royal Gunpowder Factory, patented a new method for the nitration of cotton which has been used at Waltham Abbey since 1905. The apparatus consists of sets of four circular earthenware pans, 3 feet 6 inches in diameter and 10 inches deep at the side, with a slight fall towards the centre of the bottom. They are furnished with perforated false bottoms, and are connected at their lowest points with a lead pipe provided with a stopcock, which leads to the acid supply pipes, the waste acid pipe and the waste water pipe. The pans are covered by aluminium hoods with fume pipes. The process is as follows: 650 lbs. of nitrating acid of the composition 70·5 p.c. H_2SO_4, 21 p.c. HNO_3, 0·6 p.c. nitrous acid, and 7·9 p.c. water, adjusted to a temperature of from 10° to 15°, is run into one of the pans, and the charge of 20 lbs. of cotton is gradually added and pushed below the surface of the acid. The contents are then covered with a perforated plate in sections, a flow of water carefully run over the plate, and the fume hoods removed. When nitration is complete, after about 2½ hours, water is slowly run over the surface of the acids in the nitrating vessel, and by opening the stopcock the acids are allowed to be displaced at an equal rate of about 17 lbs. per minute. Most, about 80 p.c., of the waste acid is allowed to flow back to the store tanks, where it is revivified with strong nitric acid and Nordhausen sulphuric acids, the remaining weaker acid being denitrated and concentrated. When the whole of the acid is displaced, which takes about 3 hours, the water allowed to run off through the guncotton, d the latter, after draining, is apparently al, and is ready for the boiling process. e yield in this process is about 170 p.c. of e cotton nitrated, and the product is more enly nitrated than by the Abel process.

The advantages of the displacement process e that the cotton is dipped more quickly, that e processes of dipping, nitration, removal of aste acid, drowning, and water centrifugating e conducted more quickly, and in one appara s, that there is no loss of product by occasional fuming off,' that the exposure of workmen o fumes is done away with, that there is less loss of acid, and the recovered acid is cleaner, that less water is used, that the cost of labour and upkeep of apparatus is considerably reduced, and that the yield is higher, and the product is more uniform and stable.

The improved stability of the product is attributed by MacDonald (J. Soc. Chem. Ind. 1911, 251) to the fact that unstable nitro-compounds are decomposed during the displacement, as evidenced by a rise in proportion of nitric acid in the displaced acid, after a fall, towards the end of the process.

De Brailles (Fr. Pat. 364349, 1906) has patented a system of concentrating the acids in the nitrator by electrolysis. Voigt (U.S. Pat. 855869, 1907) disintegrates the cotton fibre before nitration by immersing in sulphuric acid with only 3 p.c. nitric acid at 2°, and ultimately obtains the nitrocellulose in the form of a fine powder.

Boiling.—After the nitration and preliminary washing, the guncotton is 'boiled' in order to purify and stabilise it. The impurities removed are the last traces of free acid and unstable products of the nitration. Amongst the latter are ill-defined unstable bodies, such as nitrosaccharoses, formed by the action of the nitrating acids on the impurities in the cotton, and cellulose esters, other than the higher nitrates, such as the sulphuric esters, mixed nitrosulphuric esters, and possibly nitrous esters and low nitric esters. The possibility of the presence of sulphuric esters in unstabilised nitrocotton was pointed out by Cross and Bevan in 1901; and Hake and Bell examined their mode of formation and influence on the stability of nitrocellulose (J. Soc. Chem. Ind. 1905, 374; 1909, 457). Hake and Bell conclude that mixed sulphuric esters exist in all products of the nitration of cellulose, and that they are formed owing to delayed nitration, caused by partial solution or gelatinisation of the cellulose by sulphuric acid and subsequent fixation by nitric acid. The amount of sulphuric acid normally fixed during nitration is about 1 p.c., but this is reduced during the stabilisation to about 0·1 to 0·3 p.c.

Will found that the stability of nitrocellulose was increased by increasing the amount of water in the nitrating mixture, whilst insufficient washing lowers the stability, and that the stability decreases with increase of nitrogen content. The degree of comminution of the cotton was found to have but little effect on the stability, which was contrary to the opinion generally held at the time as to the value of the pulping process in effectively stabilising guncotton, and he also found that there is a limit to the boiling process, beyond which there is no increase in the stability.

Berthelot, in 1900, pointed out the possibility of the formation of nitrous esters, and Lunge and Bebie have examined their influence on the stability of nitrocellulose (Zeitsch. angew. Chem. 1901, 539). The nitrous esters are probably partly formed in the nitration process, but to a larger extent by subsequent hydrolytic decomposition of the nitrocellulose. They are so unstable that they very rarely occur in the finished nitrocellulose.

In the old Abel process, the guncotton received two boilings by means of steam in wooden vats, the water being separated by centrifugal machines after each boiling. In many factories, a 2 p.c. solution of soda was used in order to reduce the time of boiling, the function of the alkali being not so much to neutralise residual traces of acid as to decompose and dissolve unstable impurities; but this was found to decompose the guncotton, and was abandoned in England, and water only used. The boiling was subsequently extended; several boilings were used, and the boiling process sometimes lasted 4 or 5 days in all. At Waltham Abbey, previous to the introduction of the displacement process, a system of twelve short boilings of gradually increased duration was practised.

Robertson (J. Soc. Chem. Ind. 1906, 624), as the result of numerous experiments at Waltham Abbey, in 1905, with displacement guncotton, found that boiling in dilute acid at the beginning of the process is superior to an alkaline treatment for the elimination of impurities. He found that good results were obtained when the wash water contained acid equal to 1 p.c. of H_2SO_4 on the guncotton present, and sufficient should be left in the guncotton to give this result. At Waltham, the water is hard and the dissolved chalk makes the water sufficiently alkaline for the subsequent boiling. He also found that a better yield and a more stable product was obtained by longer periods in the early, and shorter periods in the later, boilings, and that a displacement washing at an early stage was beneficial. As a result of Robertson's experiments, the Waltham Abbey system of boiling was for some time a series of two 12, five 4, and three 2 hours' boiling, with a cold-water washing after each of the first two boilings. At the present time a still shorter period of boiling has been introduced without affecting the stability of the product.

The best system of boiling for any particular factory has to be determined by trial, and depends on the nature of the product and of the water supply. Too prolonged boiling causes loss of nitrogen and increase in the percentage of the lower nitrates constituting soluble nitrocellulose (Bruely, Mem. des Poudres et Salpêtres, 1895–6, 131).

In some factories stabilisation is effected by carrying out some of the boilings with water made very slightly alkaline with sodium carbonate, and in the United States official method of stabilisation the water is made just alkaline for the pulping and the first of the poaching operations, but not in the preliminary boiling. Delpech (Fr. Pat. 441541, 1912) claims to obtain a more stable product by treatment of the washed product with a current of carefully neutralised superheated water in an autoclave.

Many suggestions have been made for improving on the boiling process for stabilising guncotton. Luck and Cross claim that, for the production of nitrocellulose for industrial purposes, washing with dilute acetone stabilises more quickly than the ordinary boiling process. Haddan (Eng. Pat. 5830, 1900) claims that heating for 6 hours with water under pressure at 135° is equivalent to 100 hours' ordinary boiling. Du Pont (U.S. Pat. 724932, 1903) suggests agitating with water and air under pressure and suddenly releasing the pressure; and Selwig and Lunge (Fr. Pat. 327803, 1902) introduce steam into the pulped guncotton whilst it is being rotated in centrifugals, and claim that stabilisation is very rapidly effected in this way.

Pulping.—The next operation to which the guncotton is subjected is that of pulping, which is done by means of a slight modification of the machine like that known as 'the beater,' which is used in paper making for pulping rags. The pulping takes 5 hours, and has to be so conducted that the pulp is not too coarse nor too fine. The reduction in the length of the fibres allows of the last traces of acid being washed out of the fibre canals. Guttmann first introduced live steam into beaters, and so enabled the previous boiling to be considerably reduced. In modern beaters, the water is constantly renewed during the pulping, and the pulp is frequently pumped over a strainer or 'knotter,' to remove large pieces. After pulping, mechanical impurities are removed from the guncotton, usually by passing the guncotton suspended in a large bulk of water, through long troughs in which the grit settles, and is caught in traps, and over electromagnets to remove any particles of iron.

Poaching.—The guncotton is then led into large oval tanks called 'poachers,' each holding about 10 cwts. of guncotton and 1100 gallons of water, in which a paddle wheel rotates and keeps the pulp in agitation. The pulp is washed at least three times, being allowed to settle, and the washing water containing suspended impurities removed by a skimmer between each operation.

Moulding and pressing.—The treatment in the poacher serves not only to complete the washing, but also to thoroughly mix the products of a large number of nitrating operations, thus securing uniformity of product. If the pulp passes the heat test after this treatment, it receives an addition of alkali sufficient to leave in the finished guncotton from 1 p.c. to 2 p.c. alkaline matter, calculated as $CaCO_3$. By means of vacuum pressure, the pulp is then drawn up into the 'stuff chest,' a cylindrical iron tank, large enough to hold the contents of one poacher, and in which revolving arms keep the pulp uniformly mixed with the water, so that it can be drawn off as required to be moulded into cylinders and slabs. The requisite quantity of suspended pulp is found by means of small measuring tanks, and is run into moulds of the required size and shape. The moulds have bottoms of fine wire gauze, through which a large part of the water is sucked from the pulp by evacuation. Hydraulic pressure of about 34 lbs. per square inch is then applied, which squeezes out some of the water, and gives sufficient consistency to the guncotton to allow of careful handling. The mass is then removed to the press-house, and there subjected to powerful hydraulic pressure of about 5 to 6 tons per square inch.

Those slabs and cylinders which are to serve as primers (*i.e.* which are dried and receive the fulminate charge, and by their own detonation cause that of the moist guncotton) have holes bored in them while moist, to receive the tube of the detonator; and the slabs of wet guncotton may be sawn, or turned on a lathe to any required shape. Primers are dried at a low temperature and usually waterproofed by dipping momentarily in acetone or molten paraffin. No alkali is added to guncotton when it is to be used for the manufacture of smokeless powders.

Hollings (Eng. Pat. 23449, 1899) has patented a process of compression whereby large blocks of guncotton, such as are required as a charge for large shells and torpedoes, can be made in one piece of uniform density.

Testing: Moisture is best determined by placing the sample over sulphuric acid until it is of a constant weight.

Ash.—2 grams are heated with about 10 grams of paraffin wax, added as a restrainer, first on a water-bath till the guncotton has soaked up the wax, then gently over a flame until the mass inflames. The source of heat is then removed, and when the flame dies out the residual carbon is burned off as usual. The ash is recarbonated.

Alkalinity.—10 grams are well shaken with an excess of decinormal hydrochloric acid, allowed to settle, and the excess of acid determined in an aliquot portion of the clear supernatant fluid with standard alkali.

Soluble nitrocellulose.—5 grams of the sample are well shaken for some time in a stoppered cylinder with 200 c.c. of a mixture of 2 parts of ether and 1 part of alcohol, of 0·83 sp.gr., and allowed to settle. An aliquot part of the clear solution is drawn off, carefully evaporated in a platinum dish, and the residue dried at a temperature not above 50°.

Unconverted cotton.—5 grams are well shaken for some time in a conical flask with a large bulk of acetone, and allowed to settle. The clear liquid is decanted off, the residue diluted with acetone, filtered on a tared paper, washed, and dried. The ash is then determined and deducted. Boiling with a solution of sodium sulphide is frequently used instead of solution in acetone.

Nitrogen is determined by nitrometer (with 100 c.c. bulb and graduated to 150 c.c.), 0·5–0·6 gram is dissolved in about 5 c.c. of 96 p.c. strong sulphuric acid in the cold, washed into the nitrometer with a further 10 c.c. of acid, &c.

Heat test.—The dried guncotton should withstand the Abel heat test (*see Stability tests*) at 76·6°C. (170°F.) for at least 10 minutes.

Properties.—Guncotton is an odourless, tasteless, and neutral solid, having an absolute (*i.e.* when freed from air) specific gravity of 1·66 at 15·6°. The apparent specific gravity (*i.e.*

ith the included air) of dry compressed Walam Abbey guncotton at 15·6° is about 1 or little higher than 1; even after very conderable pressure, a density higher than 1·4 nnot be obtained. When dry, guncotton is adily electrified by friction.

Guncotton retains the structure of the untrated cotton. Under polarised light, nitrotton exhibits colours which both Chardonnet nd Liebschütz state are determined by the itrogen content, but De Mosenthal and Lunge nd that Chardonnet's colours are not always nfirmed, the colour depending not only on the itrogen content, but also on the method of reparation. Lunge, however, states that blue lours are characteristic of nitrocellulose conining upwards of 12·75 p.c. nitrogen. De osenthal gives the refraction, μ_D, of guncotton, 13·5 p.c. nitrogen, as 1·5059, and confirms ignon in his statement that guncotton is extro-rotatory.

Guncotton is insoluble in hot and cold ater, alcohol, ether, glacial acetic acid, and xcept the collodion cotton content), in a ixture of alcohol and ether. It is also inluble in nitroglycerin. It is readily soluble acetone, ethyl acetate, amyl acetate, nitroenzene, &c.

Guncotton is not attacked by dilute acids. ut it slowly dissolves in strong sulphuric acid ith the formation of cellulose sulphate and liberation of nitric acid. Strong nitric acid violently oxidises, and may inflame, guncotton. Dilute alkalis, especially ammonia, and alkaline carbonates, decompose guncotton slowly, especially when warm. Even chalk influences guncotton unfavourably, but it is the least unsatisfactory of the neutralising agents added to guncotton, and quantities up to 2 p.c. have no appreciable effect on the stable life of a wet guncotton; its neutralising effect on any acid liberated during the storage of guncotton outweighs its slight saponifying action.

Silberrad and Farmer (Chem. Soc. Trans. 1906, 1759) have examined the hydrolysis of guncotton in alkaline solution. They find the reaction complicated by the reduction of some of the nitrate to nitrite, and the degradation of the cellulose to hydroxy- acids, &c.

Guncotton is reconverted into cotton by the action on it of alcoholic potassium sulphydrate. This reaction, due to Hadow, was found by Abel (*l.c.*) to give 53·6 p.c. to 55·4 p.c. cotton; trinitrocellulose should give 54·54 p.c. cotton. This reaction is of great importance, as it shows that guncotton (like nitroglycerin) is a nitric ester, yielding on reduction the hydroxylic body from which it was formed, and not an amino derivative.* It can therefore be represented as:

$$C_6H_7O_2(ONO_2)_3$$

Air-dried (air under ordinary conditions) guncotton retains between 1·5 and 2 p.c. of moisture. In this condition, on application of flame, a cylinder of compressed guncotton burns in the open air very rapidly with a long and fierce flame without smoke; the flame being coloured yellow by the sodium salts. The rate of combustion of the guncotton varies with its condition: thus, guncotton plait in the form of a flat tube burns very much more quickly than guncotton yarn. When dry and heated to about 100°, guncotton burns with almost explosive violence. The guncotton, as it leaves the hydraulic press, contains about 15 to 17 p.c. water, and is then not combustible; when held in a flame, it only smoulders as it partially dries.

Briskly heated in small quantity in the form of loosely twisted yarn, guncotton was found to explode at 150° (Abel). The exact ignition point varies with the physical condition of the guncotton and the method of determination.

Guncotton can be exploded by percussion; but when struck by an iron hammer on an iron anvil, the portions directly struck by the hammer detonate, but the rest of the guncotton remains unexploded. Wooden boxes containing dry compressed guncotton, both closely and loosely packed, have been repeatedly fired at from rifles, the result being that the contents of the box were generally inflamed, but never exploded; while similar packages containing dynamite or other nitroglycerin preparations were always violently exploded by being fired at (Abel, Trans. Roy. Soc. 1874, 359–362). The use of moist guncotton has rendered any danger from shock still more remote.

Properly stabilised guncotton is a safe and permanent explosive when stored under normal conditions, especially when wet; many samples, well over 30 years old, have shown practically no signs of deterioration. Wet guncotton stored in air-tight vessels, especially wooden ones, is liable to the formation of fungoid and mould growths on its surface. The guncotton is frequently dipped in a weak alkaline solution of phenol to prevent these growths.

Under certain conditions, as when stored in contact with organic substances at rather elevated temperatures, guncotton may be decomposed by denitrifying bacteria, with the production of ammonia, nitrogen, and carbonic acid.

Products and heat of combustion. Guncotton does not contain sufficient oxygen for complete combustion into CO_2, H_2O, and N; the equation

$$2C_6H_7O_2(NO_3)_3+9O=12CO_2+7H_2O+6N$$

shows that cellulose trinitrate requires 24·3 p.c. more oxygen for complete combustion. Carbonic oxide and hydrogen are, therefore, naturally to be expected in quantity in the gases of combustion.

In the flaming combustion of guncotton, when the gases were allowed to escape freely at nearly atmospheric pressure, Sarrau and Vieille found a large quantity of nitric oxide, NO, in the gases; about one-fourth of the volume of the dry gases.

When the guncotton is inflamed in a closed vessel, in which the gases of combustion cause a moderate pressure, no oxide of nitrogen is formed. Von Karolyi exploded guncotton, in quantities of 10 grams, in small cast-iron cylinders of such strength as just to yield to the pressure of the gases produced by the combustion. These cylinders containing the guncotton were made air-tight, provided with the means of inflaming the guncotton by an electrically heated platinum wire, and enclosed in a spherical shell of about 5 litres capacity, which was exhausted before the explosion, and in which the permanent explosion gases of the guncotton produced an excess of pressure of about half an atmosphere, which enabled portions of the gases to be removed, by means of a stopcock, for analysis. Von Karolyi found the permanent gases to consist of CO_2 28·5, CO 39·8, CH_4 9·0, H 4·4, N 17·4 volumes per 100 (Pogg. Ann. April, 1863). Abel repeated Von Karolyi's experiments, and found acetylene always present in considerable quantity in the gases; an analysis of the permanent gases obtained from 10 grams of guncotton in two different experiments is given:--

Experiment 1: CO_2 19·69, CO 39·87, C_2H_2 7·85, CH_4 3·45, H 15·82, N 13·32 vols. per 100.

Experiment 2: CO_2 18·97, CO 41·80, C_2H_2 6·36, CH_4 3·87, H 17·02, N 11·98 vols. per 100.

Sarrau and Vieille (Compt. rend. 90, 1058) have ascertained the volume (at 0° and 760 mm.) and the composition of the permanent gases produced by the explosion of guncotton in a closed vessel, and find that both vary with the density of the charge $\left(\frac{\text{volume of guncotton}}{\text{capacity of vessel}}\right)$, *i.e.* with the pressure ensuing on the explosion. The following are some of the results obtained:—

	Density of charge	Volume of gases (at 0° and 760 mm.) given by 1 gram guncotton
(1) . .	0·01	658·5 c.c.
(2) . .	0·023	670·8 ,,
(3) . .	0·2	682·4 ,,
(4) . .	0·3	—

Composition of the gases per 100 volumes.

	(1)	(2)	(3)	(4)
CO_2 . .	21·7	24·6	27·7	30·6
CO . .	49·3	43·3	37·6	34·8
H . .	12·7	16·2	18·4	17·4
N . .	16·3	15·9	15·7	15·6
CH_4 . .	none	trace	0·6	1·6

With these higher pressures, equivalent to higher temperatures, the composition of the gases is simpler; they contain neither acetylene nor oxide of nitrogen, and with increase of pressure there is increase of CO_2 and H and decrease of CO; oxidation of CO by H_2O evidently occurring, and the composition of the gases being the result of a balance between the oxidising action of H_2O on CO, and of the reducing action of H on CO_2.

Sarrau and Vieille, using Berthelot's formula for guncotton, equate its decomposition by explosion thus: $C_{24}H_{29}(NO_2)_{11}O_{20}$:

(*a*) When density of charge is 0·023:

$$=15CO+9CO_2+11H+9H_2O+11N;$$

(*b*) When density of charge is 0·3:

$$=13CO+11CO_2+15H+7H_2O+11N;$$

the reaction with high density of charge (which would be the condition in actual use) tends to approach the result:

$$(c)\ 12CO+12CO_2+17H+6H_2O+11N$$

The agreement of the equations with the results of analysis is, however, only moderately approximate.

For equation (*a*) the calculated quantity of heat evolved for constant pressure (for constant volume, the quantities of heat are about $\frac{1}{100}$ higher), and the volume of the gases reduced to 0° and 760 mm. (per 1 kilogram of dry and ash-free guncotton), are as follows, compared with Sarrau and Vieille's experimental values:—

	Quantity heat calculated	Calories found	Volume gas calculated	Litres found
Water, liquid	1076	1071	684	687·5[1]
Water, gaseous	997·7	—	859	—
For equation (*c*):				
Water, liquid	1074	—	743	—
Water, gaseous	1022	—	859	—

Guncotton, therefore, on explosion, gives (for equal weights) more gas and a greater quantity of heat than gunpowder or mining powder, more gas but a smaller quantity of heat than nitroglycerin.

The heat evolved by the complete combustion of guncotton in oxygen gas, and under constant pressure, was found by Sarrau and Vieille to be per 1 kilogram of guncotton 2302 kgm.-degrees when the water formed was liquid, 2177 when gaseous.

Noble (Lecture to Inst. Civil Engin. April 3, 1884) obtained more permanent gases from detonated pellet guncotton than did Sarrau and Vieille with low densities of charge. Thus he states that 1 kilogram of guncotton (containing 2·36 p.c. moisture and 0·36 p.c. ash) produces, at 0° and 760 mm. pressure, about 730 litres of permanent gases (water, liquid); or, per 1 kilogram of dry and ash-free guncotton, about 750 litres of permanent gases. The gases were produced in the steel explosion vessel under very high pressure. The volume of gases agrees fairly well with that calculated for Sarrau and Vieille's equation (c) for high density of charge.

Noble states that the *temperature* of explosion of guncotton is at least double that of gunpowder; the latter temperature he estimates for ordinary English gunpowder at about 2200°.

The composition of the gases produced by the detonation of dry and of moist guncotton is given on p. 64.

Detonation.—Nobel, in 1864, had discovered that nitroglycerin could be *detonated* by means of mercury fulminate; and in 1868, Abel found that air-dry compressed guncotton (like nitroglycerin) could be *detonated* by the explosion in close contact with it of 5 grains (0·32 gram) of mercury fulminate, contained in a thin metal case (Trans. Roy. Soc. 1869, 159, 498). He subsequently (*ibid.* 1874, 337–395) found that by increasing the strength of the envelope, viz. by making the case for the fulminate of stout sheet iron, and inserting it in a closely fitting hole in the guncotton, the latter could be detonated with certainty with only 2 grains (0·13 gram) of the fulminate. In practice, however, much larger quantities of fulminate are used, in order to have a good initial detonation, and to provide for the possibility of the detonator tube fitting too easily into the hole in the guncotton.

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[1] 671 litres from guncotton containing 2·4 p.c. ash.

The explosion of the guncotton thus caused that of the fulminate has been called *detona-* on account of the loud sound by which it followed; it differs from the flaming combus- n of guncotton by the immensely greater ed at which chemical action (oxidation of one t of the compound, the C and H, by another t, the NO_2) progresses in the guncotton, and the consequent powerful mechanical effects duced by the gases formed. Abel found the ocity of detonation of air-dry compressed ncotton to be about 18,000 feet per second; nsequently, the large volumes of heated gases oduced at this great rate work destructively nearer objects, and give rise to a condensed ave in the air, propagated with great velocity. oreover, the air offers resistance to the motion the gases produced at so great a rate, conse- ently the gases exert pressure on the gun- tton and on the ground or other support on hich it rests, producing powerful reaction fects.

For the detonation of unconfined guncotton y mercury fulminate, it is essential that the rmer shall be in a condition to offer resistance the shock of the fulminate, so that the ergy of the shock shall heat the guncotton, ot disperse it. Compressed guncotton meets is requirement, while in the form of wool or ose yarn it is scattered or inflamed, but not tonated.

Threlfall (Phil. Mag. 1886, 172) thus gives erthelot's views on the theory of detonation: The kinetic energy of the shock of the explo- on (by the detonator) is transformed into heat the point (of the explosive) struck: the tem- rature of this point is thus raised to the tem- rature of explosion, a new shock is produced hich raises the temperature of the neighbour- ng portions to the same degree; they then ex- lode, and the action is thus propagated with n ever-increasing velocity.' The 'ever-increas- ng velocity' must refer to the commencing tage of the detonation, as Abel's measurements f the rate of detonation of guncotton and ynamite do not bear it out.

The detonation of guncotton is transmis- ible across an intervening air-space which aries with the weight of the charge; thus the detonation of a ½ lb. cylinder of compressed guncotton, 3 inches in diameter, will cause the detonation of another similar cylinder placed on the ground at a distance of 1 inch, but not at a distance of 2 inches.

Silver fulminate is in no way superior to mercury fulminate in causing the detonation of guncotton. Nitroglycerin, nitrogen chloride and iodide show a remarkable want of reciprocity in their behaviour to guncotton as regards detonation. Thus, while the detonation of ¼ oz. of guncotton caused the simultaneous detonation of a charge of nitroglycerin in a tin-plate vessel at the distance of 1 inch, and ½ oz. produced the same result across an air space of 3 inches, 1 oz. of nitroglycerin detonated in close contact with a disc of compressed guncotton did not detonate it, but only dispersed it. 100 grains of dry nitrogen iodide was unable to cause the detonation of a pellet of dry compressed guncotton on which it rested; and 50 grains of nitrogen chloride (covered with a film of water and contained in a thin watch-glass resting on the guncotton) was about the minimum quantity required to effect the detonation of the latter (Abel, Trans. Roy. Soc. 1869, 489).

With increase in the amount of water in the compressed guncotton, more mercury fulminate is needed to effect detonation; the fulminate as usual being contained in a tin-plate tube and fitting closely in a central hole in the guncotton. With a total of 5 p.c. of water (*i.e.* 3 p.c above the 2 p.c. of normal air-dry guncotton), detonation by 15 grains of mercury fulminate is doubtful. Moist guncotton containing 12 p.c. water was detonated only once in seven experiments by a detonator containing 100 grains of fulminate; when the guncotton contained 17 p.c. water, it required 200 grains of fulminate to detonate it with certainty.

Guncotton as it leaves the press, containing about 15 p.c. water, although quite uninflammable, can be readily exploded by the detonation in contact with it of about half an ounce of air-dry compressed guncotton. For the certain detonation of guncotton containing 20 p.c. water, a primer of about 1 oz. of dry guncotton is required: and when the guncotton has absorbed the maximum amount of water it is capable of doing (30–35 p.c.), for its certain detonation 4 ounces air-dry guncotton applied in close contact are necessary (Abel, Trans. Roy. Soc. 1874, 337). This discovery (which was due to Brown, of Woolwich Arsenal) has been of the greatest practical importance, as it has rendered the use of guncotton for military purposes very safe; permitting the great bulk of the guncotton to be kept in a moist and uninflammable state, while a relatively small quantity only of dry guncotton is needed for 'primers,' the dry primers being detonated by a suitable mercury fulminate detonator.

The velocity of detonation of moist guncotton is greater than that of the dry, and the work done by the same weight of guncotton appears to be equal, whether it be employed in the dry or moist state.

As in the case of dry guncotton, detonation is propagated in masses of moist compressed guncotton in contact, provided the piece first detonated does not contain less water than the others; but for transmission of detonation in the open air through any considerable number of cylinders or slabs of moist guncotton, it is essential that they should be in contact, much shorter air spaces than in the case of dry guncotton stopping the detonation.

The rate of detonation of moist guncotton is a little quicker than that of dry guncotton; and that of guncotton saturated with water (containing about 30 p.c. of it) is considerably quicker than that of the dry. Abel (Roy. Soc. 1874) measured (by means of Noble's chronoscope) the rate of detonation of guncotton under different conditions, of dynamite, and of nitroglycerin.

Cylinders of compressed guncotton 3 inches in diameter were employed; they were placed on their bases, and, when in a continuous train, with their circumferences touching, and the measurements of velocity of detonation were made at intervals of 6 feet, or sometimes of 4 feet, in the train of guncotton. The following are some of the results obtained:—

	Rate of progression of the detonation: feet per second		
	First 6 feet	Last 6 feet	Mean (of all the measurements)
Dry guncotton, 170 cylinders, touching	17,466 4 feet	17,738 4 feet	17,122
" " ½-inch air spaces, 28 feet	15,676 4 feet	16,218 4 feet	16,776
Moist guncotton (15 p.c. water), 28 feet, touching .	18,416	18,040	18,375
Wet guncotton (30 p.c. water), 36 feet, touching .	22,574	19,240	19,948
Dry guncotton, containing 38 p.c. KNO_3, touching .	—	—	15,981

The above results show that there is a decided increase in the rate of detonation of guncotton, when the air in the latter is replaced by the very slightly compressible water—a behaviour recalling the greater velocity of propagation of sound in water than in air.

The velocity of propagation of sound, too, comes nearest to the detonation-velocities just given; thus the experimental values for sound (of low intensity) in water at 8° is 4708 feet per second, and in ice is 9512 feet.

Wet guncotton, when frozen, is detonated with certainty by the fulminate detonators ordinarily used for dry guncotton (Abel, *v. supra*).

The gases resulting from the detonation of dry and of wet compressed guncotton were examined by Noble and Abel, and from their results the two following analyses are taken. The detonation was effected in a very strong steel explosion vessel, in which the gases were formed under very great pressure. A correction should be made in the dry guncotton gases for the permanent gases (2CO+2N) of the mercury fulminate detonator, and for the same and those from the small quantity of dry guncotton priming in the case of the wet guncotton gases; but as the CO would be oxidised by the gaseous water to an unknown extent, the direct results are given.

Composition of the permanent gases, vols. per 100.

	Dry guncotton, 1620 grains pellet, 130 grains mercury fulminate detonator	Wet guncotton
CO_2 .	24·24 . .	32·14
CO .	40·50 . .	27·12
H .	20·20 . .	26·74
N .	14·86 . .	14·00
CH_4 .	0·20 . .	none
	100·00	100·00

It is noticeable that Sarrau and Vieille's results for the composition of the gases of explosion of guncotton for the lower density of charge (*v. supra*) approach the composition of these detonation gases of dry guncotton. The influence of the additional water on the gases of detonated wet guncotton, in oxidising CO to CO_2 with formation of H, is very marked.

For the condition of gaseous water, a greater quantity of heat will be evolved by the detonation of dry guncotton than by that of moist guncotton containing the same weight of the dry material; the volume of the gases will, however, be greater from the moist than from the dry guncotton. The volume of the permanent gases also will be greater with moist guncotton, owing to the H formed from the water.

Von Forster, in Germany, for special military use, coats pieces of moist compressed guncotton with a skin of dry guncotton by immersing them for about a quarter of a minute in ethyl acetate.

It has also been proposed to use paraffined guncotton instead of moist guncotton, prepared by immersing dry compressed guncotton in melted paraffin. The paraffin has the advantage over water that it does not evaporate; it is said to make dry guncotton less sensitive to shock, but it lowers the percentage of oxygen, and is stated to be inflammable.

Intensity of action.—Abbot, in his Report, gives the intensity of action of compressed guncotton, detonated under water, as 87, kieselguhr dynamite No. 1 being 100. In comparative experiments made in this country, under different conditions to Abbot's, guncotton has shown a slightly greater intensity than dynamite; as, for instance, in the displacement of earth by the detonation of buried charges, and in the work of excavation done by their detonation in the borehole of lead cylinders. Abel's experiments, by the latter method, give the intensity of action of guncotton as 101, the dynamite being 100; experiments in which the same weight of fulminate was used being compared.

Uses.—Guncotton is almost exclusively employed for military purposes, for use in offensive torpedoes and in submarine mines, and for demolitions on land. It is also used in the manufacture of smokeless powders, both military and sporting, and in certain fuses and fuse compositions.

Guncotton mixtures. It has already been mentioned that 100 lbs. $C_6H_7O_2(NO_3)_3$ require 24·3 lbs. additional oxygen for complete combustion into CO_2 and H_2O; and guncotton, on account of the lower nitrates present, would require more oxygen. At an early period in the history of guncotton, this oxygen was supplied in the form of potassium or other nitrate. Potassium chlorate was also suggested but abandoned, owing to the lack of stability of the mixture, although the explosive effect of the guncotton was largely increased.

Potentite is a mixture of guncotton and potassium nitrate.

Tonite, invented by Trench, is manufactured by the Cotton Powder Co. at Faversham, and also at San Francisco. It was originally intended to be used as a propellant, but is now only used as a disruptive explosive. *No.* 1 is an intimate mixture of about equal weights of wet guncotton pulp and barium nitrate, the paste being compressed into cartridges with the usual recess for the detonator, and wrapped in paraffined paper. *No.* 2 is a mixture of guncotton, potassium and sodium nitrates, charcoal, and sulphur; and *No.* 3, a mixture of 18–20 p.c. guncotton, 11–13 p.c. dinitrobenzene, and 67–70 p.c. barium nitrate, and 0·5–1 p.c. moisture. Tonite was used in the construction of the Manchester Ship Canal. *No.* 1 is used for blasting hard rock. *No.* 3 is slower in its action, and is used for soft rocks. It is also used for military purposes.

Tonite burns slowly and without tendency to explosion on ignition. It detonates readily and completely, and there is practically no carbonic oxide in the products of detonation.

Abel found its intensity of action, by the lead cylinder method, to be 84, kieselguhr dynamite No. 1 being 100.

Abbot (Addendum I. to his Report) examined tonite of San Francisco make, consisting of 52·5 p.c. guncotton and 47·5 p.c. barium nitrate. Detonated under water, it gave intensity 81, dynamite being 100.

Whilst the intensity is lower than that of guncotton, these values show that the guncotton is remarkably economised in tonite. To render tonite safe for use in fiery mines, the cartridges are surrounded by a layer of 'Trench's Fire-extinguishing Compound.' This is sawdust impregnated with a mixture of alum, ammonium chloride and sodium chloride, and extinguishes all flame from the tonite on detonation of the latter.

Other guncotton mixtures are included under 'Smokeless Powders.'

Collodion cotton.—By collodion cotton, for the purposes of explosives, is meant soluble nitrocotton. It is less highly nitrated than guncotton, and at the present time is looked upon as a mixture, in varying proportions, of the di-, tri-, tetra-, and penta-nitrocelluloses of Eder's classification.

It is possible to prepare soluble nitrocotton of a definite nitrogen content, by working under definite conditions as to composition of acid mixture, and temperature, and time of nitration. For smokeless powders and the gelatin dynamites, a nitrocellulose soluble in nitroglycerin or other solvents, containing as high a percentage of nitrogen as possible, 12·5 to 12·7 p.c., is desirable, and also one capable of holding the nitroglycerin bound, so that it does not exude under varying climatic conditions. The limit of nitrogen permitted by H.M. Inspectors of Explosives in collodion cotton for gelatinous explosives is 12·3 p.c., and the usual content 11·5 to 12 p.c.

Manufacture.—In the manufacture of collodion cotton, the finer qualities of white cotton waste are used. The mixed acids are much weaker than in the manufacture of guncotton, and the temperature of nitration is higher. Lunge, however (*l.c.*), found that the quality of the cotton, provided that it has not been altered by drastic chemical or heat treatment, had little or no effect on the quality of the collodion cotton obtained. He also concludes that 40° is the most suitable temperature for obtaining a maximum yield of maximum degree of nitration and solubility, and that the maximum content of nitrogen in the product is obtained when the ratio of sulphuric acid to nitric acid is not less than 0·25 : 1, and not more than 3 : 1.

The acid mixture usually used contains about 66 p.c. H_2SO_4, 23 p.c. HNO_3, and 11 p.c. H_2O; and the nitration is usually carried on for between 1 and 1½ hours at a temperature of about 40°. To obtain a completely soluble nitrocotton it is best for the acid mixture to contain sufficient water to form $HNO_3 \cdot H_2O$ and $H_2SO_4 \cdot H_2O$, but slightly more water is usually present. However, the exact acid mixture and temperature and time of nitration vary considerably in different factories, and sometimes collodion cotton is made in the cold by using an appropriate nitrating mixture.

The nitration is performed in either lead or iron nitrating pots or tanks, or in centrifugals and the extraction of acid, washing, pulping, and other processes are carried out in the same way as with guncotton, except that in the production of collodion cotton for gelatinous explosives it is usual to soak the nitrocotton in water at about 90°, instead of submitting it to a boiling process.

Claessen has claimed (D. R. P. 163688, 904) the preparation of a nitrocotton completely soluble in alcohol of 96 p.c. by vol. strength, by nitrating cotton with 30 times its weight of a mixed acid containing 35–45 p.c. HNO_3, 35–46 p.c. H_2SO_4, and 18–20 p.c. H_2O at a temperature of 40°–50°.

Properties.—Collodion cotton should be completely soluble in ether-alcohol and in nitroglycerin. It is also soluble in the solvents of guncotton. Bernadou states that when collodion cotton is immersed in ether and kept at a temperature below 0°, it passes into solution or forms a colloidal jelly. Its exploding temperature is higher than that of guncotton, and its explosive effect much less.

Collodion cotton, besides being used in the manufacture of smokeless powders and the gelatinous dynamites, is sometimes used in other explosive mixtures. For example, the Soc. Universelle d' Explosifs (Fr. Pat. 432863, 1910) suggests an explosive containing 'liquid trinitrotoluene,' gelatinised with collodion cotton at about 40°–50°, incorporated with three times its weight of a perchlorate, or a mixture of ammonium perchlorate and ammonium nitrate.

Partially soluble nitrocotton. Nitrocottons intermediate in nitrogen content between that of guncotton, of about 13 p.c., and that of completely soluble nitrocotton, of about 12 p.c. or less, are required for certain smokeless powders. These are manufactured by varying the conditions of nitration, composition of nitrating acids, proportion of acid to cotton, and time and temperature of nitration, or sometimes by carefully blending the requisite proportions of guncotton and soluble nitrocotton.

Lunge showed that guncottons with more than 13·5 p.c. nitrogen are unstable, and Mendeléeff, by nitrating at a comparatively high temperature, obtained a soluble nitrocellulose containing as much as 12·5 p.c. nitrogen, and this was adopted for use in the manufacture of

Russian military smokeless powders. A nitrocotton of similar composition is also used by the United States Government. This nitrocotton has been called *Pyrocollodion*, and, as Mendeléeff pointed out, is approximately of the composition required for the conversion of all its carbon to monoxide on explosion.

Smokeless Powders.

History.—Attempts were made by the inventors and early workers in guncotton, notably in Austria, to adopt it as a propellant. Schönbein and Otto, in 1846, attempted to use guncotton in rifles, and von Lenk, in 1862, prepared cartridges of spun and woven guncotton for use in cannons. The guncotton was much too rapid and violent in its action, even when woven or compressed, and none of these early experiments was successful.

Abel, in 1865 (Eng. Pat. 1102, 1865), patented a process for granulating guncotton with a solution of gum, and also proposed to use a mixture of guncotton and collodion cotton treated with a solvent, and Kellner, of Woolwich Arsenal, at about the same time, made a granular smokeless powder from guncotton; but these powders did not get beyond the experimental stage.

A semi-smokeless powder was invented by Schultze, of the Prussian artillery, in 1865, who used nitrated wood granulated with a saturated solution of barium and potassium nitrates; and Volkmann, in 1870, who worked Schultze's patent near Vienna, treated the grains with a mixture of ether and alcohol, and practically made a modern gelatinised smokeless powder. The manufacture of this powder, however, was prohibited, in 1875, as it infringed the gunpowder monopoly of the Austrian Government. Schultze's powder was manufactured by an English company at Eyeworth in the New Forest, in 1865, and, with modifications, is still in use for sporting purposes.

The difficulty in adopting guncotton as a propellant was its porosity, for when the powder was ignited, the flame was forced into the interior of the grains, and caused the whole charge to explode, instead of burning progressively. Many attempts were made to reduce the rate of combustion by compression, and by mixing the guncotton with inert ingredients, such as unnitrated cotton, or coating the grains with paraffin, stearin, or indiarubber, and more or less successful sporting powders were produced in this way. Prentice, in 1866 (Eng. Pat. 953) suggested a sporting powder made of pyropaper, containing 15 parts of unnitrated cellulose; and Punchon proposed to regulate the speed of combustion of guncotton by soaking in a solution of sugar, and added nitrates to increase the explosive force (Eng. Pat. 2867, 1870).

In 1882 Reid (Eng. Pat. 619, 1882) patented a process for the granulation of a mixture of soluble and insoluble nitrocellulose, and hardening the grains with ether-alcohol: the product, known as 'E. C. Powder,' is too violent in its action for military purposes, but is still largely used as a sporting powder. 'J. B. Sporting Powder,' afterwards introduced by Johnson and Borland (Eng. Pat. 6951, 1885), was a mixture of collodion cotton with potassium and barium nitrates, hardened by a solvent of the nitrocellulose and subsequent drying.

Some form of military smokeless powder became essential on the introduction of small-bore magazine rifles, and efforts were again made in 1885 to retard and regulate the combustion of nitrocellulose by converting it into a product absolutely devoid of all porosity. The sporting powders in use at the time were only superficially hardened, and contained fibrous nitrocellulose, but eventually Vieille, in 1886, introduced 'Poudre B,' named after General Boulanger, a completely gelatinised, dense, horny, and non-porous explosive, made by treating a mixture of guncotton and collodion cotton with ether-alcohol, the resulting paste being rolled into thin sheets, cut into small squares, and dried, and this was adopted by France as a propellant for the Lebel rifle.

Other countries at once began to work on similar lines, and Germany adopted a similar powder, in 1889. But Nobel, after the invention of blasting gelatine, tried to utilise nitroglycerin as an ingredient for a smokeless propellant, and eventually patented 'Ballistite' in 1888 (Eng. Pat. 1471, 1888), a colloid mixture of collodion cotton and nitroglycerin, which at first also contained camphor. This powder was adopted by the Italian Government. About the same time, an English Explosives Committee was working on the same subject at Woolwich, and gradually evolved a nitroglycerin smokeless propellant, which was adopted by the British Government under the name of 'Cordite' (Eng. Pats. 5614, 1889; and 11664, 1890). Cordite is a mixture of guncotton and nitroglycerin, with a small proportion of mineral jelly. A nitroglycerin powder similar in composition to cordite was adopted by Austria-Hungary in 1893.

Some form of smokeless powder was rapidly adopted by all civilised countries for small-arm purposes, and since that time the manufacture, composition, and form of the explosives have been gradually modified and so perfected that, at the present time, accurate and reliable smokeless powders are available and solely used as propellants even for the heaviest ordnance.

The general principle in the manufacture of all these smokeless powders is to thoroughly gelatinise the nitrocellulose by means of some solvent, so that its fibrous character is destroyed.

The powders are more or less hard, homogeneous colloids, which only burn progressively from the surface, so that their combustion is completely under control. They are never absolutely smokeless, as even if they give no solid products of combustion, the steam produced always gives a smoke varying in amount with the atmospheric conditions.

Composition.—Smokeless and semi-smokeless powders can be roughly divided into the following classes, according to their composition: (1) Nitrocellulose powders, which may be composed of collodion cotton or guncotton or a mixture of the two. (2) Nitrocellulose powders with oxidising salts, in which one of the divisions of class (1) is mixed with a metallic nitrate, and perhaps other ingredients. (3) Nitrocellulose-nitroglycerin powders, where one of the divisions of class (1) is combined with nitroglycerin. (4) Nitrocellulose powders combined with another nitro derivative, with or without nitroglycerin and metallic nitrates.

Military smokeless powders.—The desirable properties in a military smokeless powder are numerous. It should be smokeless and flameless, should not cause erosion of the bore of the gun, or leave any quantity of residue, particularly of a corrosive nature. It should be readily and uniformly ignitable, and should burn in such a way that the pressure should be slowly developed and well sustained whilst the projectile is in the gun, but no unconsumed powder should be projected from the muzzle. It should give products of combustion as free as possible from combustible gases, for example, carbon monoxide, as these tend to ignite at the muzzle of the gun and give a ' back-flash,' which may be dangerous. It should give a high muzzle velocity without excessive pressures, and it must give accurate firing results, as a result of uniform internal ballistics. It should be chemically and physically stable under all practical conditions of storage, so as neither to become dangerous nor give irregular, and possibly dangerous, pressures. It should be insensitive to variations in atmospheric temperature and moisture, and not be affected by being fired from a hot gun chamber. Some of these properties are more necessary than others. It is impossible to combine all the desirable properties in one propellant, and all propellants in use are compromises, according to their use.

A completely gelatinised powder burns away in layers from the ignited surface, the rate of burning varying directly with the pressure. In the open the powders burn rapidly but quietly, but in the closed chamber of a gun the products of combustion soon raise the pressure, and explosive burning is soon reached. The rate of burning of a complete charge of given composition depends on the size, shape, and consistency of the grains, ignition of the grains usually taking place simultaneously over their entire surfaces. The shape of grain should be such that it gives as large a burning surface as possible until the combustion is complete. A cubical or spherical shape is, therefore, of the worst type, a rod-shaped grain is a little better, but either a long tubular grain or large flat strip is better still, as the burning surface is then practically the same at the end as at the beginning of the combustion. Flat strips, however, give irregular ignition at times, owing to the way the strips pack together. For large calibre guns a multi-perforated grain is best, as the burning surface increases as the grain burns away, but if the grains are too long they are liable to break up during burning. Some modern ' progressive propellants ' are so manufactured that the interior material has a more rapid rate of burning than the surface layers. The rate of combustion may be tamed or moderated by chemical as well as by physical means. Although powders belonging to all the above classes have been tried for sporting purposes, and many of them also for military purposes, so far as the latter are concerned, there are to-day only two varieties of smokeless powders, nitrocellulose powders and nitrocellulose-nitroglycerin powders.

The smokeless powders of the latter class are more powerful than the pure nitrocellulose powders, for the nitroglycerin supplies the oxygen, that is deficient in guncotton, for complete combustion. A smaller charge and consequently a smaller gun chamber are necessary with the nitroglycerin powders for equal ballistic results. The solvent is more readily eliminated when the powder contains nitroglycerin, and the powders are cheaper; but the temperature of combustion is higher, and, with a large proportion of nitroglycerin, the consequent erosion of the gun is serious. The erosion can be minimised by the inclusion of a moderant in the composition, such as the 5 p.c. of mineral jelly in cordite and the metallic nitrates in certain sporting powders. The nitroglycerin powders are decidedly more stable than the pure nitrocellulose powders. Nitrocellulose powders tend to give irregular ballistics, owing to their sometimes more porous nature and frequent physical instability on storage, and sometimes quite a small proportion of nitroglycerin is added to remedy this defect. They also have a relatively rapid rate of decomposition on storage, but this may be counteracted to some extent by the use of a stabiliser. Their great advantage, particularly for small arms, machine and quick-firing guns, is that they are relatively cool burning, and give considerably less erosion than the nitroglycerin powders.

Nitrocellulose powders are, at the present time, generally made entirely or largely of soluble nitrocotton, otherwise acetone has to be used for complete gelatinisation, and the finished grains are then harder and more brittle, particularly if the elimination of the solvent is carried too far. These tend to break up on storage or in the gun, and give irregular ballistics, and sometimes dangerous pressures. Nitrocellulose powders containing much insoluble nitrocotton are sometimes used, as in France, but they are incompletely colloided by the ether-alcohol used as solvent, are more porous, and are liable to gain or lose moisture, according to the storage conditions, with consequent irregular firing results. Generally, the powders with lowest normal moisture content are least prone to alteration of this content with varying storage conditions. The nitrocellulose powders are more bulky than the nitroglycerin powders.

Secondary ingredients.—Besides the main ingredients, nitrocellulose and nitroglycerin, military smokeless powders usually contain small quantities of other substances added for attaining some special purpose. These secondary ingredients may be added as moderants or deadeners, stabilisers, or cooling agents.

Moderants or deadeners are added to reduce or control the rate of combustion of the explosive. Amongst these substances may be mentioned camphor, vegetable oils, such as castor oil; and mineral hydrocarbons, such as paraffin and vaseline.

Stabilisers.—The addition of a small quantity of alkali was frequently made in the early days of smokeless powders to combine with any acid developed in them on storage. This addition of alkaline neutralising agents was, however, soon shown to be harmful, because they are liable, under certain conditions, to hydrolyse the nitro-compounds.

This is true even of [illegible] mild an alkali as calcium carbonate. Alkaline neutralisers yield nitrites, which decompose again at elevated temperatures, and so act catalytically in decomposing the nitrocellulose.

Residual solvent was found to stabilise the powders to a considerable extent by absorbing the products of decomposition; and to prevent rapid loss by evaporation, solvents of high boiling-point were used, for instance, a little amyl alcohol was added to an ether-alcohol solvent. The elimination of the solvent leaves the powder porous and so accelerates the rate of decomposition.

The more usual method of stabilising is to add a small quantity of some substance that will form a stable compound by chemically combining with any liberated peroxide of nitrogen, and so act so long as any of the free substance is left. Aniline, diphenylamine, aminoazobenzene, nitroguanidine, phenanthrene, the higher alkyl derivatives of the anilides of organic acids, and similar compounds are added for this purpose. The vaseline in cordite, although originally added for another purpose, has been proved to have a marked stabilising influence. Soaps, resins, and oils have also been suggested as stabilisers.

The French Commission, on the explosion of smokeless powder on the 'Jena' in 1907, drew attention to the fact that substances like diphenylamine and aniline not only act as stabilisers, but also as *indicators* of decomposition, owing to the formation of local spots or patches of peculiar colours, and such substances have been increasingly used for this purpose since that time.

Cooling agents.—Most smokeless powders have a high temperature of explosion, which not only causes erosion of the bore of the gun, but also gives a strong and readily visible flame. The more complete the combustion, the higher the temperature of explosion, and simple alteration of proportions of the ingredients of a nitroglycerin and nitrocellulose explosive, so as to render the combustion less complete, will give a lower temperature and less flame, as is instanced by 'modified cordite.' The substances added as moderants (metallic nitrates, oils, fatty and mineral, wax, resin, camphor, &c.) tend in the same direction, and the addition of charcoal has also been proposed. With these additions, the products of combustion contain more carbonic oxide and hydrogen, and the actual temperature of explosion is less. The addition of a sufficient quantity of these substances to adequately reduce the temperature of explosion frequently causes a serious reduction of the explosive power, and in some cases is objectionable through rendering the grains brittle. The 5 p.c. of mineral jelly in cordite effects a considerable reduction of the temperature of explosion without serious effect on the ballistics, for, although the temperature is reduced, the volume of gas is increased. The use, in comparatively large quantity, of substances like guanidine nitrate, nitroguanidine, and substituted ureas, has been claimed to reduce the temperature of explosion without reducing the ballistics of the powder.

With incomplete combustion, however, the carbon monoxide and hydrogen inflame on coming in contact with the air, and, burning together with any unburnt charge, produces a very decided flame. To produce a *flameless explosive*, substances are added so as to mix the products of explosion with a sufficient proportion of non-inflammable gas to protect the inflammable gases from the atmosphere until their temperature has fallen below their ignition-point. The problem is similar to the production of a safety detonating explosive for use in fiery coal-mines, and similar remedies have been proposed.

Duttenhofer (Eng. Pat. 24782, 1904) proposed the addition of an alkaline bicarbonate, claiming that it had no detrimental effect on the stability of the explosive, as is the case with the normal carbonate. It cools the flame by the liberation of its water of crystallisation and carbon dioxide. In a later patent, Luciani (Fr. Pat. 380963, 1906) proposes a mixture of carnauba wax, bees-wax, and sodium bicarbonate. Edwards (Eng. Pats. 24025, 1907, and 12188, 1908) proposes a similar mixture, in which the sodium bicarbonate may be replaced by the ammonium or magnesium compounds; and Vender (Fr. Pat. 405822, 1909) claims for hydrated magnesium carbonate or manganese peroxide. Sodium resinate and other sodium and potassium salts have been suggested, but these give more smoke on firing. Oxalic acid and its salts have also been tried, but a really suitable ingredient for decreasing the flame of smokeless powders in guns of large calibre has however not yet been found.

Solvents.—The solvents used in the gelatinisation of smokeless powders are usually acetone, ethyl acetate or amyl acetate for guncotton powders, and a mixture of ether and alcohol for the collodion cotton powders.

Powders gelatinised with ether-alcohol are very liable to blister, curl up, and become distorted during drying, owing to the rapid evaporation of the ether, and there is difficulty in driving off the amyl acetate owing to its high boiling-point. The correct proportion of solvent has to be carefully worked out for individual powders. Too much solvent increases the difficulty of drying, and increases the liability to distortion and cracking, whilst too little delays the mixing and renders it imperfect.

The secondary ingredients are usually dissolved in the solvent before it is added to the main ingredients.

Heating with camphor under pressure, instead of treatment with solvents, gelatinises and hardens soluble nitrocellulose powders, but this substance, as it remains as a constituent, causes physical instability owing to its volatility, and its use has been abandoned. The use of phenyl benzoate, or an ester of a homologue of phenol, for the colloiding of soluble nitrocellulose has been patented by the Dupont de Nemours Company (U.S. Pat. 1161863, 1915). The solvents used in the gelatinisation do not, as a rule, remain in the finished powders except in very small quantity.

Manufacture.—Only a general outline of the manufacturing processes is given here: the details vary, and some are given under individual powders.

The drying of the nitrocotton.—In this country some 30 p.c. of water is left in the nitrocellulose in its finished condition as a safety measure. The nitrocellulose, either loose or, for convenience in handling and to prevent dust, lightly compressed into cylinders or slabs, is dried by exposure on tiers of copper- or brass-gauze trays in well-constructed and well-isolated wooden huts or 'stoves' by means of a current of dry air forced in through a series of holes at the top of the stove and leaving through openings near the floor (the moisture-laden air falls as the temperature is lowered by the evaporation of the water), the temperature in the stove being kept at about 40°. The drying takes up to several days according to the degree of compression of the nitrocellulose. This is one of the most dangerous operations in the manufacture of smokeless powder, especially when the last portions of the moisture are being driven off. Any dry dust is very susceptible to ignition by friction or shock, and the dry nitrocotton is readily electrified even by a current of dry air, and special precautions have to be taken to connect the drying trays to earth, the necessity for which was first pointed out by Reid. The nitrocotton must be cooled down before unloading the stove, as it is more susceptible to ignition by friction or percussion whilst hot, and the stoves are specially constructed to avoid the accumulation of dust. The nitrocellulose is sometimes dried by removing part or the whole of the water by treating it with alcohol. This process was used in 1891 in Austria, and was patented in England by Durnford in 1892. To render the nitrocellulose anhydrous, it is first soaked in alcohol that has been previously used, squeezed and pressed, and then treated similarly with fresh alcohol. When ether-alcohol is to be used as the gelatinising agent of the nitrocellulose, displacement of the water by alcohol is now the usual method of eliminating the water, and this method is in general use in the United States and on the Continent. The nitrocotton is packed into the cylinder of a hydraulic press and alcohol forced through it. Water is at first forced out, then a weak alcohol, which is collected and rectified by distillation, and finally only slightly weakened alcohol, which is used again for the preliminary displacement of another cylinder of wet nitrocotton. The nitrocotton is then submitted to a higher pressure, so as to leave only sufficient alcohol in the mass for its gelatinisation on admixture with ether. Dehydration by alcohol is carried out in some factories by spraying the alcohol over the nitrocotton packed to form a layer over the basket of a centrifugal. A further advantage of this process is that unstable impurities are eliminated by this washing with alcohol. Berl and Deply (Zeitsch. Ges. Scheiss- u. Sprengstoffw. 1913, 8, &c.) have examined the impurities extracted by the alcohol in the dehydration of nitrocotton, and, besides a small quantity of inorganic impurities derived from the wash waters, find them to consist of a sticky brown mass of lowly-nitrated organic matter of poor stability and low ignition point.

Mixing and incorporating.—The nitrocellulose should be in as fine a condition as possible. The first wetting with the solvent is a difficult matter, and is sometimes effected *in vacuô*. The absence of all dust, when once the solvent is added, makes the manufacture of smokeless powders much safer than that of gunpowder. Even if ignition occurs, the combustion, though fierce, never leads to explosion, and is usually very local in its effects. The introduction of alcoholising the wet nitrocotton in the manufacture of nitrocellulose powders renders their manufacture a safe one from the beginning, except for fire risk.

The incorporation is usually carried out in kneading machines, but sometimes by rolling. The kneading machine almost exclusively used is that of Werner, Pfleiderer, and Perkins. It consists of an iron trough, the upper part of which is rectangular. The bottom is in the form of two parallel half-cylinders, in which two heavy screw-shaped paddle-blades revolve in opposite directions, one at about twice the rate of the other. The allowance between the blades and bottom is small and the mixture is thoroughly kneaded and mixed between them and the trough. Some of the solvent is first introduced, then the nitrocellulose and any other ingredients, and finally the remainder of the solvent. The incorporation takes some hours for completion, and at the end the trough is tilted, and the direction of rotation of the blades reversed, the finished 'dough' being thrown out and caught in a suitable box with a lid for transference to the rolling or pressing house. The mass becomes considerably heated during the kneading, and to prevent loss of solvent, the machine is covered and the bottom is surrounded by a cold-water jacket. It is necessary to connect the mixing machines to earth, as in the case of the drying trays.

When the material is to be worked into sheets, the rolling is sometimes effected in two operations, the first to effect incorporation of the materials, and then between closer set rollers to reduce the sheets to the requisite thickness. For powders of the ballistite type, the rollers are hollow and steam heated. The sheets are then dried to drive off greater part of the solvent, and again rolled to eliminate any blisters formed during the drying. Thick sheets are produced by folding the thin sheets over and over and passing them backwards and forwards between the rolls, by which means a homogeneous thick sheet is obtained. In the manufacture of strip and flake powders it is now more usual to incorporate as usual and press the dough through a suitable die to give a ribbon of the required thickness and width, which is subsequently cut into suitable lengths for drying.

Cutting and pressing.—The partially dried sheets are usually cut into small square plates. The machines generally used are similar to those in use at the German Government factory at Spandau, in which two sets of revolving circular cutting knives, slightly overlapping, cut the sheet into strips, which are then fed over a fixed cutting edge, and chopped into plates or cubes by a set of rotating knives. Round flakes and discs are cut from cords. After cutting, the grains are further dried. For the preparation of spherical grains the pasty mixture is cut into small fragments, frequently cylinders cut from cords, dried superficially, and then rolled over a rapidly oscillated heated surface.

Cord and tube powder is usually pressed through dies, as in the manufacture of cordite, the material being sometimes subjected to a preliminary rolling to exclude air bubbles, but the Austrian rifle powder is stated to be drawn and not pressed. For producing the tubular and multi-perforated powders, one or more pins are arranged so as to project into the holes of the dies. When long perforated tubes are to be manufactured, the pins of the dies are tubular, so as to admit air into the powder perforations, otherwise there is a tendency for the tubes of powder to collapse.

Drying.—The powders are dried slowly in stoves, at a temperature of about 40° C. The time of drying depends on the size and shape of the grains, but usually lasts several days. In modern factories, the drying stoves are air-tight, and the current of hot air is drawn, by means of fans, through special apparatus for recovering the solvent. In some cases, the solvent is largely eliminated by boiling the shaped powder in water. The Dupont de Nemours Company (Fr. Pat. 477343, 1915) suggest drying smokeless powders by heating the grains in oil at about 100° C., the liberated solvent being condensed and recovered, and the oil subsequently removed from the surface of the grains by washing with acetone.

One of the drawbacks of pure nitrocellulose powders is the difficulty of eliminating the solvent in a reasonable time, especially from the larger sizes, without causing the development of cracks on the surface of the grains. Sometimes a rather large proportion of solvent is left in the powder, but then on storage the solvent evaporates, and cracks may also form and so render it impossible to attain the constancy of ballistics necessary in a military powder. The solvent can be more easily removed from nitroglycerin powders, and the higher the percentage of nitroglycerin the more rapidly and more efficiently can the solvent be eliminated.

The flake small-arm powders are usually graphited, so that the grains may run freely through the cartridge-loading machines.

Blending.—To ensure uniformity of ballistics, the different batches of powder are thoroughly blended.

Sporting smokeless powders have the advantage over black powder that they gives less recoil and less noise. They may be broadly divided into two classes—bulk powders and condensed powders.

The bulk powders have a low density, and are designed so that a charge may have the same bulk as black gunpowder to give the same velocity and pressure, and so that the standard 12-bore paper cartridge, of 2½ inches nominal length and holding 3 drams of gunpowder by measure, needs no alteration. They are used mainly in shot guns, and only to a limited extent in sporting rifles. Relatively to military powders, they are required to be quick-burning, and are consequently not so completely gelatinised. The grains are loose and only surface hardened by means of a solvent. They are usually composed of soluble nitrocellulose, or a mixed nitrocellulose containing about 12·5–12·8 p.c. nitrogen, incorporated in the usual mill with a mixture of barium and potassium nitrates. Usually about 7 parts of barium nitrate are used to 1 part of potassium nitrate, but sometimes barium nitrate is used alone. Barium nitrate has the advantage that it is not hygroscopic and yields very little smoke, but it has a disadvantage in leaving a residue in the gun that is difficult to remove. A small proportion of vaseline, or paraffin wax, is sometimes added as a moderant. Starch is used occasionally to help in the agglomeration of the grains, and camphor was at one time used to help the gelatinisation. Mononitro- and dinitro-benzenes and toluenes are present in some powders to moderate the action, and assist the gelatinisation. Lamp black, wood meal, various gums, and potassium ferrocyanide have also been used as ingredients, and a small proportion of calcium carbonate has been added for stabilisation. The mixture is usually granulated either by sprinkling with water and rotating in a drum or by spreading out on a rapidly oscillating table, but sometimes the mixture is slightly compressed and afterwards broken up into grains, which are then sifted and dried. In all cases, the solvent is sprinkled over the powder after granulation. The manufacture of these powders is described in detail by Glaser (Eng. Pat. 23105, 1892), and by Jones (Eng. Pat. 1154, 1897).

The bulk powders are graded according to the number of grains weight that are equivalent to the 3 drams measure of black powder. The original standard charge was 42 grains, to-day 33 grains is the most common, but there are also 38-, 36-, and 30-grain powders.

The condensed powders have a high density, and the charge occupies only one-third to one-half that of a gunpowder charge. They are used in cartridges with a false base of coned paper, or in smaller cartridges in specially designed modern weapons. These powders are completely gelatinised, and are made in a similar way to the military flake small-arm powders. The requisite rate of burning is obtained by suitable adjustment of size and shape of the grains. The powder paste is rolled into thin sheets, which are cut up into small flakes, and the grains dried as usual.

Occasionally sporting powders are made by an intermediate process, the grains being thoroughly gelatinised. The powder, wet with solvent, is treated with steam, so that the solvent rapidly evaporates and leaves the grain in a bulky form, but the nitrocellulose is hardened throughout the mass, and waterproofed.

Properties.—Pure nitrocellulose powders are grey to yellow, and nitroglycerin powders yellow to brown in colour. They are sometimes coloured by the secondary ingredients, or dye substances may be added, and the grains, more especially those of smaller size, are frequently coated with graphite, giving them a grey to black colour. The surface is usually smooth, but sometimes matted. The powders usually have the consistency of horn, but those containing nitroglycerin are softer and more readily cut than the pure nitrocellulose powders. The specific gravity of the powders varies with their composition and mode of manufacture, but the gravimetric density of the small flakes or grains is usually between 0·25 and 0·40.

The shape of the grains varies considerably. Sporting powders are usually in grains or very thin flakes; military small-arm powders either in thin squares, rectangular plates or discs, or in small cubes, thin cords, or narrow ribbons. The powders for large guns may be in the form of ribbons, thick cords, round or square sectioned, large cubes, tubes, or cylinders, the size and shape of the grain being adapted to any particular-sized gun, so that the highest possible muzzle velocities may be obtained without excessive pressures. The larger the grain, the less the initial burning surface per unit weight, and the slower burning the charge. The thicker cords and cylinders are frequently perforated through their length by one or more fine holes. The length of the perforated cords must not be too great, or they break up into fragments under the pressure developed in a gun, and the excessive pressures developed may burst the gun. If very long, tubes will even burst when fired in the open. Sometimes long perforated cords have transverse cuts or perforations made in them at intervals to facilitate the escape of the gases and prevent the bursting.

Irregularity of ignition causes irregular burning and pressures. Flakes, strips, and sheets may ignite and burn irregularly, owing to the grains adhering together. To prevent this irregular ignition and burning, the flakes are frequently cupped, or the edges scalloped or grooved, and the strips and sheets have grooves cut in them, or have ridges or small projections moulded on their surface. Fully gelatinised powders give a surface that is less favourable for ignition than the more porous powders. Rough edges on the grains or strips facilitate ignition, but if not normally present and allowed for, may lead to too rapid ignition and abnormally high pressures. Schmidt (D. R. P. 286784, 1913) proposes to give a hardened rough surface suitable for ignition by first gelatinising the outer layers of the pressed grains in a bath of acetone, and then degelatinising the surface by dipping in a bath of benzene, or light petroleum.

To obtain slow initial burning of the grains and low initial pressures, powders with delayed ignition and progressive rate of burning have been introduced. The grains are sometimes coated with a deterrent, either a non-explosive, such as graphite or a wax, or a semi-explosive like dinitrotoluene. The idea of *delayed ignition* was patented by Jones (Eng. Pat. 15553, 1898), and was a most important step in the development of smokeless rifle powders. He suggested the use of a wax, or a mixture of waxes, a solid hydrocarbon of high melting-point, solid substances, like dinitrotoluene, which have, when melted, a solvent action on the substance of the grain, or of graphite mixed with a small quantity of oleaginous substance. In the *progressive propellants* the grains are built up of layers of different rates of burning, the inner layers having the higher rate. In the Dupont powders this result is attained by regulating the processes of manufacture so as to close the minute pores with the result that the density of the grains is very high in the surface layers, and gradually decreases towards the interior. These powders are very cool burning, and not so hygroscopic as ordinary nitrocellulose powders, and give a marked increase of muzzle velocity without increase in chamber pressure. Progressive powders are made at Röttweil by impregnating the surface layers of the grain with 'centralite,' dimethylphenylurea, as a restrainer, and in other powders of this class the grains are impregnated by soaking in a weak solution of paraffin wax in benzene.

Stability, physical and chemical, under all conditions of climate, storage, and use, is one of the most desirable qualities in a military explosive. Smokeless powders usually contain small quantities of moisture or residual solvent. This has a considerable influence on the shooting qualities of a powder, and has to be carefully regulated in quantity. The effect of excess of solvent, especially on the nitrocellulose powders, in causing physical instability has been already pointed out. Pure nitrocellulose or nitroglycerin-nitrocellulose powders are not affected by moisture, but all nitrocellulose powders are subject to slight deterioration on storage, the deterioration being a function of the temperature, increasing with rise of temperature. The chemical stability of military powders is tested on manufacture and at frequent intervals (*see Stability tests*). Nitroglycerin powders may exude nitroglycerin on cold storage, but it is usually re-absorbed at normal temperatures.

Smokeless powders require smaller charges and gun chambers to produce equal velocities with black gunpowder, and the pressures are more slowly developed and better sustained whilst the shot is in the bore of the gun. This gradual development of the pressure depends on their colloidal nature; the grains when ignited only burn in successive layers, even under the high pressures developed in a gun. An ideal propellant should have a low maximum pressure, slowly developed and maintained so long as the projectile is in the bore of the gun, and should be completely consumed at the moment the projectile leaves the bore.

The regularity of the shooting of smokeless powders, after regularity of ignition, depends on the purity of the materials and the perfection of the manufacture. All powders are carefully blended, and subjected to analysis and a test for pressures developed and velocities obtained before acceptance.

Smokeless powders are very insensitive to shock and percussion; they are not fired by the passage of a bullet through them. Even those powders with a high percentage of nitroglycerin cannot be detonated by means of a strong detonator, unless there is much unabsorbed nitroglycerin present. They are somewhat difficult to ignite, and sometimes ignite irregularly, owing to their horny nature and smooth surface. Small-arm powders require more powerful caps than black gunpowder, and the larger charges require priming with gunpowder or guncotton to make ignition certain. The ignition point of gelatinised nitrocellulose powders is about 175°–180°, and of nitroglycerin-nitrocellulose powders about 180°–185°, when the temperature is raised rather rapidly. The ignition point is lowered by heating up slowly, and even a trace of acid has a considerable effect in lowering the ignition-point.

The solid residue from smokeless powders and its effect on the formation of rust in small arms has been examined by van Pittius (Zeitsch. angew. Chem. 1906, 848). He found that a graphited pure nitrocellulose powder gave about 0·11 p.c. of a faintly alkaline residue. The matter insoluble in water was 0·01 p.c., and contained graphite, oxides of copper and iron, and traces of antimony sulphide. The soluble residue, 0·1 p.c. on the powder, contained 17 p.c. potassium ferrocyanide, 17 p.c. ammonium carbonate, 13 p.c. ferric chloride, 31 p.c. potassium carbonate, 10 p.c. calcium chloride, 7 p.c. copper sulphate, and 5 p.c. potassium antimoniate. The residue contained no nitrates, nitrites, chlorates, cyanides, or sulphides. A graphited nitrocellulose-nitroglycerin powder, 40 : 60, gave about 2 p.c. of a faintly alkaline residue of which only about $\frac{1}{50}$th was insoluble in water, and contained graphite and oxides of iron and copper. The soluble residue contained 51 p.c. potassium carbonate, 38 p.c. potassium chloride, 11 p.c. potassium antimoniate, and traces of iron and sulphate. There were no nitrates, nitrites, chlorates, cyanides, ferrocyanides, sulphides, or ammonium salts present. In the residues, the antimony, potassium, sulphate, and chloride, actually come from the cap composition, the iron largely from the gun and the copper from the bullet.

After experimenting with various solutions, Pittius concludes that the residue from the powders are not in themselves rust producers, but become so after a time, as they are hygroscopic. Frequent washing out of the gun and subsequent oiling with a viscous lubricant will be sufficient to prevent rusting.

The erosion of the bore of the guns caused by smokeless powders is almost entirely conditioned by the temperature developed in their explosion, and not to any corrosive action of the products of combustion. It is greater with the powders containing nitroglycerin than with the pure nitrocellulose powders.

The gaseous products of combustion of smokeless powders are water vapour, carbonic acid gas, carbonic oxide, hydrogen, nitrogen, and a small quantity of marsh gas. Sometimes oxides of nitrogen are formed when the explosion is imperfect. They may be always produced at the moment of explosion and be subsequently reduced by the large volume of carbonic oxide and hydrogen at a high temperature.

The heat of explosion and products of combustion of several commercial varieties of smokeless powder have been determined by the ordinary calorimetric bomb method, by Macnab and Leighton, and the following table showing some of their results is taken from a paper read by them before the Society of Chemical Industry, in March, 1904 (J. Soc. Chem. Ind. 1904, 298) :—

Powder	Calories per gram	Permanent gas per gram 0° and 760 mm	Water vapour c.c. per gram	Total gas c.c. per gram 0° and 760 mm.	Percentage composition of permanent gas				
					CO_2	CO	CH_4	H	N
Imperial Schultze	742	763	152	915	8·9	52·7	1·0	27·0	10·4
Amberite . .	745	635	156	791	12·0	50·0	0·4	25·5	12·1
S.S. . . .	755	695	131	816	11·8	51·3	0·8	23·7	12·4
E.C. . . .	762	718	158	876	11·9	52·1	0·5	23·9	11·6
Schultze . .	786	576	160	736	15·5	46·7	0·8	23·0	14·0
Kynoch's smokeless	807	600	126	726	14·8	49·5	0·7	18·8	16·2
Cannonite . .	845	725	146	871	14·6	49·9	0·6	22·2	12·7
Shot-gun rifleite .	896	705	169	874	19·0	45·3	0·8	21·5	13·4
Walsrode . .	1014	669	206	875	21·3	48·2	0·4	10·1	14·8
Cordite M.D. .	1031	726	215	941	16·3	50·4	0·0	19·7	13·6
Cordite . .	1253	647	235	882	24·9	40·3	0·7	14·8	19·3
Sporting ballistite	1286	591	234	825	32·2	37·1	0·4	10·1	20·2

Under the conditions of the experiments no oxides of nitrogen were formed. The authors call attention to the fact that the quantity of heat developed in the nitrocellulose powders increases with the nitrocellulose content, and that a large increase takes place when nitroglycerin is present. Other conclusions are, that as the heat increases, the quantity of carbon dioxide increases, the carbon monoxide and hydrogen decrease, and a larger quantity of water vapour is formed.

The relative temperatures of explosion of these powders were determined by a thermoelectric pyrometer method described by Macnab and Ristori in 1900 (Proc. Roy. Soc. 66, 221). The order of the powders according to the temperature developed was, broadly speaking, the same as that given by the total heat of combustion.

The constants of explosion of several smokeless powders have been exhaustively examined by Noble, showing their relationship to the density of loading (*see* Proc. Roy. Soc. 1905, 381, 512 and 1906, 453). With the density of charge varying from 0·05 to 0·50, Noble found that, as a general rule, with increase of resulting temperature and pressure, there was at first a slight increase and then a steady decrease in the volume of the permanent gases, also a large increase in the volume of CO_2 and decrease in the volume of CO. The volume of H decreases with increasing pressure, while that of CH_4 rises rapidly. He also found that the amount of erosion depended almost entirely on the heat developed, and was independent of the pressure.

Only a few smokeless powders can be referred to in any detail. With many powders the details of composition and manufacture are desired to be kept secret; and of the details characteristic of any powder, only those are given which have been already published.

The military smokeless powders, especially, are constantly undergoing modifications and improvements and frequently different compositions, nitrocellulose or nitrocellulose-nitroglycerin powders of different degrees of nitration and proportions, are in use at the same time by a country for military purposes, according to the calibre of the gun in which they are to be used, and according as the powder is required as a propellant or for blank ammunition

At the present time most countries use nitrocellulose powders, usually of the same composition, but differing in form of grain, for small-arm purposes and for field guns, and in the United States, France, and Russia they are used even for the largest naval guns England, Italy, and Norway use nitroglycerin powders generally, and most other countries use them for large naval guns.

(1) *Nitrocellulose Powders.*

Poudre B., or Vieille powder, was the pioneer of military smokeless powders. As invented by Vieille, in 1886 (Mém. des Poudres et Salpêtres, 1908–9), it was a mixture of soluble and insoluble nitrocellulose, thoroughly gelatinised with a mixture of ether and alcohol, rolled into sheets and then cut into strips. It sometimes contained about 2 p.c paraffin. It had a nitrogen content of about 12·7 p.c For a short time a smokeless powder containing metallic nitrates was adopted in France, but eventually a pure nitrocellulose with a little stabiliser was adopted for general use. Amyl alcohol was tried as a stabiliser in proportions of 2 p.c., and later 8 p.c., in the powders B.AM$_2$ and B.AM$_8$, but diphenylamine was afterwards used. The nitrocellulose used in the manufacture contains about 40 p.c. soluble nitrocellulose, and as used is a mixture in the requisite proportions of an insoluble nitrocotton CP$_1$ (coton poudre). containing about 12·8 to 13·1 p.c. nitrogen, and a soluble nitrocotton CP$_2$ containing about 12 to 12·5 p.c. nitrogen. These nitrocottons are manufactured alternatively by one of the three usual processes, and after the usual washing, boiling, and pulping are dehydrated by alcohol. In the incorporation per 100 parts of nitrocotton 140 to 150 parts are used of a mixture of 1·9 vols. of ether, 65°B., sp.gr. 0·7264, to 1 vol of alcohol, 92·5 p.c. by weight, sp.gr. 0·8164, including the alcohol present in the nitrocotton after dehydration. The diphenylamine, 1·5 to 2 p.c. of the nitrocotton, is added with the solvent. The incorporation takes from 1 to 3 hours, and the 'dough' is squirted through a die, over which is a filter of fine wire gauze to remove solid impurities, to form ribbons of from 20 to 150 mm. in width, and a thickness which varies according to the calibre of the gun in which the powder is to be used. The ribbons are cut into lengths, and the strips are hung on rods in the solvent recovery chambers, where they first meet warm air containing a high proportion of vapours of ether and alcohol, and are gradually moved forward against the air current, so that they eventually meet air containing only a small proportion of solvent vapours. This prevents the strips curling up at the edges by too rapid evaporation of the solvent at first. Part of the solvent vapours is removed from the air by condensation at a low temperature, and then, after being heated up, the air passes again into the recovery chambers. After this preliminary drying the strips, which still contain 15 to 20 p.c. solvent, mostly alcohol, are cut first into narrow ribbons, then into short strips of the requisite size. Irregular grains are picked out by hand from the larger sizes, and sifted out from the small square flakes used for small arms. The sorted grains are then further dried for about 6 hours on trays in stoves at 45°-50°, then soaked, in canvas bags or wire trays, in a tank of hot water, the time of soaking being about 8 hours, and the temperature of the water about 75°, but the time and temperature vary slightly with the size of the strips. By this soaking nearly all the alcohol is eliminated. The grains are then drained and the water finally dried off in a stove. The volatile matter, water, and residual solvent, left in the powder is about 0·8 to 2 p.c. of the powder, according to the size of the grains. If dried too far, the grains are exposed to moist air until of the requisite volatile content. Finally, the grains are thoroughly blended before being made up into cartridges.

The rate of burning of the French Poudre B is controlled not only by the size of grain and content of volatile matter, but also by varying to some extent the proportions of CP$_1$ and CP$_2$ in the powder. CP$_1$ is not gelatinised by the solvent, but in the finished powder is coated by the gelatinised CP$_2$. A higher proportion of CP$_1$, consequently, gives not only greater power, because of its higher nitrogen content, but also more rapid burning, as it is ungelatinised. The presence of ungelatinised CP$_1$ renders the powders slightly porous, and consequently the moisture content varies somewhat with the conditions of storage, and the powders are also less stable on storage than the fully gelatinised powders.

E. C. powder, a bulk sporting powder, as originally invented by Reid, was a pure nitrocellulose powder, superficially gelatinised with ether-alcohol and coloured orange with aurine. The E. C. powders are now manufactured by the E. C. Powder Co. at Dartford, under the patents of Johnson and Borland, already mentioned, and contain a more highly nitrated cotton, with potassium and barium nitrates and sometimes camphor and wood meal.

Walsrode powder, one of the earliest granulated sporting powders, made by Wolff and Co. of Walsrode, is a pure nitrocellulose powder gelatinised with ethyl acetate. The grains were formed, and the solvent eliminated by adding water to the kneaded mass and introducing steam, and subsequent boiling in water; the grains were then centrifugated and dried. The granulation is now effected differently, but the essential treatment is the same. The finished powder contains about 1 p.c. of volatile matter and 98·5 p.c. of nitrocotton.

M. N., or Maxim-Nordenfelt, powder is an American guncotton powder gelatinised with ethyl acetate.

Normal powder manufactured by the Swedish Powder Co. of Landskrona, and adopted by the Swiss Government, is a gelatinised guncotton powder made in various forms. Ethyl acetate is the gelatinising solvent. The small-arm powder was at one time in the form of small, light-grey, graphited square tablets of about 1·25 mm. side, but now small cylinders, of about 1 mm. diameter and length are used. It contains about 1·5 p.c. of residual solvent, and about 95 p.c. guncotton.

Von Förster powder (Fr. Pat. 164792, 1884) and *Troisdorf powder* are gelatinised nitrocellulose flake powders, the former containing a little calcium carbonate.

Wetteren powder, made by Cooppal, and used as the Belgian Service powder, was a guncotton powder, containing a little calcium carbonate, gelatinised with amyl acetate. It was at one time a nitrocellulose-nitroglycerin powder, containing soluble nitrocellulose and about 30 p.c. nitroglycerin, the small arm powder being made into graphited cubes of about 1·5 mm. side. The Belgian Government eventually adopted a powder similar to 'Poudre B,' containing 40 to 60 p.c. soluble nitrocotton, and gelatinised with ether-alcohol. The paste was rolled into sheets and cut into strips or flakes.

The Russian Government at first used nitrocellulose powders containing various proportions of insoluble and soluble nitrocotton, but, after investigation by Mendeléeff, eventually adopted a nitrocellulose powder for both naval and military purposes made from an almost completely soluble nitrocotton containing a high percentage of nitrogen, about 12·4 p.c., termed 'pyrocollodion.' This has the advantage over the mixed nitrocottons used in France, that it is practically completely gelatinised by ether-alcohol, and gives a much more uniform colloidal product of increased stability on storage. The powder is manufactured very much on the lines of 'Poudre B,' and is stabilised with about 1 p.c. diphenylamine.

The United States service powder was at one time the *Maxim-Schupphaus powder*, composed of 80 p.c. insoluble nitrocellulose, 19·5 p.c. soluble nitrocellulose, and 0·5 p.c. urea. Another form contained 80 p.c. guncotton, 9 p.c. nitroglycerin, 10 p.c. collodion cotton, and 1 p.c. urea. These powders were gelatinised with acetone. Nitrocellulose powders with barium and potassium nitrates, and a nitroglycerin powder, were also used for a time as small-arm powders. The *modern United States powders*, for all purposes, are manufactured from a nitrocellulose containing about 12·5 to 12·7 p.c. nitrogen, about 80 p.c. being soluble nitrocotton, that is practically a 'pyrocollodion.' The nitrocotton, after the nitration and preliminary boiling, is pulped in water made just alkaline with sodium carbonate, and boiled in poachers for several periods, carbonate of soda being added only in the first period. The nitrocotton, after alcohol drying, is thoroughly colloided with ether-alcohol, stabilised with diphenylamine, and pressed into short perforated cylinders, with usually one or, for the larger grains, seven perforations, one central, and the others arranged 'symmetrically,' the multi-perforated cylinders differing in web-thickness according to the use of the powder. The method of solvent elimination and drying the grains is similar to that in use in France.

The powder used in the cartridges for the Mannlicher-Schoenauer (Austro-Hungarian) rifle is in the form of thin cupped discs, of 2 mm. diameter, lightly graphited, composed of soluble nitrocellulose, with about 1 p.c. of residual solvent. That for the Mauser (German and Turkish) rifle is of similar form and composition, except that a more highly nitrated cotton used.

The Japanese use a nitrocellulose powd containing both soluble and insoluble nitr cotton, the proportions of which vary accordir to the size of the gun in which the powder is be used; the more rapid powders, used for sma arms and guns of low calibre, containing mo of the highly nitrated cotton. The Spanish ar Dutch powders, both for small arms and lar guns, are nitrocellulose powders containir various proportions of collodion cotton ar guncotton.

(2) *Nitrocellulose Powders with Nitrates.*

Schultze powder, invented by Schultze Potsdam, and now manufactured in Englan was one of the earliest sporting smokele powders. It is manufactured from nitrat wood cellulose, sometimes called 'nitrolignin.'

Hard wood is cut into sheets and punche into grains. The wood grains are purified boiling with dilute sodium carbonate, by washi with water, and treating with solution chloride of lime. They are then washed, drie and immersed in the mixture of strong nitric a sulphuric acids for 2 or 3 hours, with freque stirring, the acids being kept cool. The nitrat wood is freed from most of the acid in a cent fugal machine, washed with water, boiled wi dilute sodium carbonate, and dried. The nit lignin appears to contain a large quantity matters soluble in ether-alcohol, and, besid insoluble nitrolignin, some unconverted wo It is steeped in a solution of potassium a barium nitrates, and dried at a low temperatu It is a fibrous, 42-grain, bulk powder contain approximately 65 p.c. nitrated cellulose, which 40 p.c. is soluble in ether-alcohol, 30 p metallic nitrates, up to 4 p.c. mineral jelly, a up to 2 p.c. volatile matter.

In later varieties, wood pulp, treated by o of the usual chemical processes to remo material other than wood cellulose, is used nitration. The nitrated wood cellulose a nitrate mixture is formed into irregular grai which are treated with a solvent to gelatin and harden them. Another form of the powd *Imperial Schultze*, consists of about 80 p nitrolignin, 10 p.c. barium nitrate, 8 p.c. vaseli and 2 p.c. of volatile matter. It is less bul than the older powder, and is said to be qu free from smoke and to leave no residue. T still more modern *Cube powder*, a gelatinis 30-grain bulk powder, and *Lightning powder*, fibrous 33-grain bulk powder, contain the sa ingredients in different proportions and diff ently manufactured.

The modern '*E. C. powders*,' manufactur by the E. C. Powder Co., as already explain belong to this class. *No.* 1 contains abo 2 p.c. resin, *No.* 2 2 p.c. resin and 1 p.c. camph and *No.* 3 6 p.c. vaseline and 4 p.c. camph The different varieties also contain differe proportions of metallic nitrates and nitrocellul of different degrees of nitration. The camp present in Nos. 2 and 3 is added in accorda with the suggestion of Johnson (Eng. Pat. 89 1885) to use a solution of camphor in a vola solvent to harden the fibrous granules. No. was hardened by ether-alcohol.

Amberite, as originally patented by Cu and Andre (Eng. Pat. 11383, 1891), was a mixture of insoluble and soluble nitrocellulose with nitroglycerin. The mixed nitrocelluloses were first granulated, and then treated with ether-alcohol, so that only the soluble nitrocellulose was dissolved, and on drying, cemented the grains together and hardened their surface. A small quantity of linseed oil, paraffin, or shellac, was sometimes added as a moderant.

Amberite, as now manufactured by Curtis's and Harvey at Tonbridge, contains a mixture of potassium and barium nitrates instead of the nitroglycerin, and a little paraffin. An analysis gave: 13 p.c. guncotton, 59·5 p.c. collodion cotton, 19·5 p.c. barium nitrate with a little potassium nitrate, 6 p.c. paraffin, and 2 p.c. volatile matter.

Cannonite, also made by Curtis's and Harvey, is a similar powder to Amberite, containing a higher proportion of nitrocellulose and a smaller proportion of nitrates, together with small quantities of potassium ferrocyanide and lamp-black. Resin was a constituent of the earlier forms.

Empire powder is a 33-grain fibrous, bulk powder, manufactured by Nobel's Explosives Co., containing insoluble and soluble nitrocotton, about 10 p.c. metallic nitrates, and 7 p.c. mineral jelly.

Neonite is a 33-grain sporting rifle powder, manufactured by the New Explosives Co., Stowmarket, containing about 10 p.c. metallic nitrates and 6 p.c. mineral jelly, the nitrocellulose being largely insoluble.

Poudre pyroxylée is a French sporting powder, containing soluble and insoluble nitrocotton mixed with about 35 p.c. barium and potassium nitrates. The mixture is incorporated with water, ether is then added, and the mixture granulated. The grains are then dried and afterwards glazed by means of an ether spray. *Poudre J.* contains about 83 p.c. guncotton and 17 p.c. potassium dichromate. *B. N. powder* was a French military powder, similar to 'Poudre B,' with the addition of barium and potassium nitrate and a little sodium carbonate.

Smokeless diamond, a gelatinised, 33-grain, bulk powder, manufactured by Curtis's and Harvey, consists largely of insoluble nitrocellulose, with about 15 p.c. metallic nitrates, 6 p.c. charcoal, and 3 p.c. mineral jelly.

W. A. powder made by the American Smokeless Powder Co., is a guncotton-nitroglycerin powder with barium and potassium nitrates. It is manufactured in the same way as cordite, but the powder for small arms is cut into short cylinders.

One form of *U.S. Naval powder* is composed of soluble nitrocellulose with barium and potassium nitrates, and a form of *U.S. Army powder* contains insoluble and soluble nitrocellulose, nitroglycerin, metallic nitrates, and a moderant. Some American small-arm powders, besides barium nitrate, contain a small quantity of starch. One form of *Belgian blank ammunition* consisted of small light-coloured grains of soluble and insoluble nitrocotton, with about 25 p.c. of barium nitrate and a little rosin.

(3) *Nitrocellulose-Nitroglycerin Powders.*

Ballistite, the first nitroglycerin-nitrocellulose powder, as patented by Nobel, was a mixture of equal parts of collodion cotton and nitroglycerin with about 10 p.c. camphor. The mixture was first made with an excess of nitroglycerin, which was afterwards removed in a press or centrifuga machine, and the mass then thoroughly incorporated by passing between steam-heated rollers—malaxation, as Nobel termed it.

In this way, nitrocotton was dissolved in the nitroglycerin, and horny, colloidal sheets of varying thickness obtained, which were afterwards cut up into thin squares or cubes. At some factories, benzene was added to assist the incorporation, and afterwards removed by drying the finished product.

Camphor, suggested to Nobel by its use in celluloid, was at first used to reduce the rate of burning, and was also found to facilitate solution of the nitrocellulose. Owing to its slow evaporation from the finished explosive, it led to variable ballistic results being obtained from the explosive, and its use was subsequently abandoned. 1 to 2 p.c. of aniline or diphenylamine is now usually added to ballistite for the purposes of stabilisation.

Ballistite is now manufactured by an improved process invented by Lundholm and Sayers (Eng. Pat. 10376, 1889). The nitrocotton, in the form of fine powder, is suspended in water at a temperature of about 60°, the nitroglycerin, in which the diphenylamine is dissolved, is added and the mixture stirred by means of compressed air. The nitroglycerin gradually displaces the water and dissolves the nitrocotton, and, when the solution is complete, the water is partly drained off and the remainder removed in a centrifugal or by pressure, and the mass allowed to ripen. The paste is then rolled under heavy pressure, between rollers, steam heated to 50°–60° to complete the incorporation and remove the last traces of water. The great advantage of this process is that the dangerous and tedious drying of the nitrocotton is done away with.

Ballistite is the Service explosive of Italy, and is used not only in small squares, small perforated cylinders, and larger cubes, but also in cords, '*Filite*,' and round flakes cut from the cords. The powders sometimes contain a little mineral jelly. Ballistite is used for certain military purposes in England, and has been adopted by some other countries specially for large guns.

Ballistite, composed of equal parts of nitroglycerin and soluble nitrocellulose, has considerable erosive effect on the gun, and for the larger guns a modified composition with a lower proportion of nitroglycerin, often 40 p.c., is used. Nitrocotton with a proportion of insoluble nitrocellulose is also sometimes used. The German cannon powders are ballistities of various compositions made into the form of thick flakes or cubes. Some of them approach cordite in composition, that is, they contain a high proportion of insoluble nitrocotton, and the grains are sometimes in the form of tubes.

Ballistite is dark-brown in colour, and has an average density of 1·6. It has the consistency of soft horn, and can easily be cut with a knife. It is but little affected by moisture, but is more susceptible to heat than most smokeless powders, the nitroglycerin tending to exude. The grains are frequently coated with graphite. It burns slowly in the open, and is almost entirely smokeless.

Cordite, the English Service propellant, is so named because of its usual cord-like form. For special purposes, however, it is made into tubes, with single or several perforations, and is sometimes used in the form of tape, and in flakes made by slicing cords.

Composition.—Cordite is essentially a mixture of nitroglycerin and guncotton, thoroughly incorporated and gelatinised by means of acetone. The guncotton has a nitrogen content of 12·8–13·1 p.c., and contains not more than 12 p.c. soluble nitrocellulose. A small proportion of mineral jelly is the third ingredient.

Mineral jelly was originally added to prevent metallic fouling of the magazine rifles by the bullets, and was also found to diminish erosion by acting as a restrainer or cooling agent, to improve the regularity of the burning, and act as a water-proofing agent.

It was subsequently found that cordite made for blank purposes without mineral jelly was considerably less stable in hot climates than ordinary cordite, and it is now recognised that the mineral jelly contains constituents, olefines and naphthenes, that stabilise the cordite for a prolonged period by combining with the products of decomposition. It also protects the nitroglycerin and nitrocotton from atmospheric influences.

The mineral jelly obtained in a particular stage of the distillation of petroleum, used in the manufacture of cordite, is required to have a flash-point above 204·5°C. (400° F.), and not to be completely melted below 30°. It must be free from acidity and mineral impurities, and have a sp.gr. of not less than 0·87 when melted at 38°.

The guncotton used for the manufacture of cordite usually contains from 10 to 12 p.c. soluble nitrocellulose.

The original cordite, the manufacture of which was commenced at the Royal Gunpowder Factory in 1890, was composed of 58 p.c. nitroglycerin, 37 p.c. guncotton, and 5 p.c. mineral jelly. The composition was the same for small-arms and for the different calibred guns for which it was used, the requisite rate of combustion being obtained by varying the diameter of the cord. Owing to its high nitroglycerin content, this cordite had a high temperature of explosion, and produced considerable erosion in guns of very large calibre, and in 1901 its composition was modified for some purposes. This modified composition, known as '*Cordite M.D.*,' contains 30 p.c. nitroglycerin, 65 p.c. guncotton, and 5 p.c. mineral jelly. The older composition is known as '*Cordite Mark I.*'; both varieties are now in use. Cordite contains practically no moisture, but retains about 0·4–0·6 p.c. of acetone, according to the size of the cords. Cordite M.D., owing to its smaller proportion of nitroglycerin, retains more volatile matter, about 0·5 to 1·5 p.c. Other modifications of cordite have also been introduced. In one a mineral jelly containing a higher percentage of unsaturated hydrocarbons is used to increase the stability of the product, and another contains soluble nitrocotton instead of guncotton. The former has the same proportions as M.D., in the latter, in order to obtain similar ballistics to those of M.D., the proportion of nitroglycerin is raised.

Manufacture: Drying the guncotton.—Formerly the guncotton was dried in a loose condition, but it is now loosely compressed into cylinders 3 inches diameter and 4½ inches high, containing about 40 p.c. moisture. Guncotton dust formed in the drying is the great source of danger, and its formation is obviated by the present method. The guncotton cylinders are dried in a stove on wire-gauze trays, by a current of air heated to about 40°, until they contain about 0·5 p.c. moisture. The drying takes from 90 to 100 hours.

Mixing.—The charge of the cooled dry guncotton, sufficient for one incorporator, is weighed out into a rubber-lined canvas bag, carried to the nitroglycerin filtering house, and the requisite charge of nitroglycerin, which was at one time weighed out, is measured out from a lead burette through a rubber tube on to the guncotton. The bag is then carried to the mixing house and the contents roughly mixed by hand and rubbed through a copper wire sieve of ½-inch mesh, or on lead-lined table perforated at one end with ½-inch holes through which the mixture is rubbed into the bag below. The product at this stage is known as '*Cordite paste*.'

Incorporating.—Part of the acetone charge is first poured into a kneading machine of the usual type, the machine started, and the cordite paste and the remainder of the acetone, about 56 p.c. of the weight of the guncotton in all, gradually added. The mixture is covered to prevent loss of acetone, and the mixture kneaded for 3½ hours. At the end of this time, the charge of mineral jelly is added, and the machine run for another 3½ hours. During the kneading, the acetone gradually dissolves the guncotton and nitroglycerin, and thoroughly incorporates them with the mineral jelly. The product is called '*Cordite dough*.'

Pressing.—The cordite dough is conveyed in barrels to the press house, where it is 'squirted' or pressed by plungers working in cylindrical moulds through a die with one or more holes, according to the diameter of the cord required. A perforated plate, supporting a fine wire gauze diaphragm, is placed above the die to retain mechanical impurities. Three kinds of presses are used at Waltham Abbey—screw presses for the smaller sizes, and hydraulic or combined screw and hydraulic presses for the larger sizes. The smaller-sized cords are wound automatically on to reels as they leave the die, the larger sizes are cut into the required lengths.

The sizes of Service cordite refer to the diameter of the cords in hundredths of an inch. It varies from size 3¾ to size 50; that is, from 0·0375 inch diameter used in the ·303 Service rifle to 0·5 inch diameter used in heavy guns. The actual diameters are rather less than the nominal sizes, as the cords shrink during drying.

Drying.—The cordite is then placed on the reels, or the larger sizes on trays, on open racks in stoves, heated by steam pipes or by a current of hot air at a temperature of about 40°. For the smallest sizes no heating of the stove is necessary in summer time. The time required for drying varies, according to the diameter of the cord, from 2 to 15 days. The drying is to remove any moisture and the greater part of the acetone, of which about 15 p.c. remains in the pressed cordite. The residual volatile matter in Mark I. cordite varies with the size of cord from 0·4 to 0·6 p.c. M.D. cordite requires a much longer time for drying than Mark I., several months' heating being necessary for the largest sizes.

A process for the recovery of the acetone has been patented by Robertson and Rintoul (Eng. Pat. 25994, 1901), in which the air, containing only a low percentage of acetone, after being saturated with moisture, is led into a scrubbing tower through which a 30 p.c. solution of sodium bisulphite trickles. The acetone is recovered by distillation at a temperature such that the bisulphite is not decomposed and can be used again.

Blending.—The cordite is finally thoroughly blended in order to obtain average uniformity of composition and ballistics. The small-arm cordite is blended by uniformly winding the cords from 10 reels on to one larger reel, and afterwards from six of these ten-stranded reels on to one sixty-stranded reel. The larger sizes are blended by hand, the sticks from the drying-stove trays being placed in boxes and the contents of these blended by combining a few sticks from each box, the operation being repeated.

Testing: Moisture.—The residual solvent or moisture is determined on the ground sample, precaution being taken to prevent loss of nitroglycerin. 5 grams of siftings of the same size as those used for the Abel heat test, are heated for 2 hours on a water-bath in an aluminium dish covered with a glass cone, both of specified dimensions (*see* Marshall, J. Soc. Chem. Ind. 1904, 154).

Analysis.—Weigh out 2 grams of very fine siftings into a Soxhlet thimble, and allow to stand covered with ether in the extractor overnight. Extract for 2 hours, then dry the thimble and contents at 50° until the guncotton can be removed to watch glasses. Dry at the same temperature till the *guncotton* is of constant weight. The extracted guncotton may be submitted to the usual tests for guncotton.

Distil off the ether from the extract and dissolve out the nitroglycerin with cold methyl alcohol, filtering the solution. Dissolve any mineral jelly on the filter with ether back into the flask, distil, heat in a water-oven, and suck out any traces of nitroglycerin vapours with an air current. Repeat till the *mineral jelly* is of constant weight. The *nitroglycerin* is usually estimated by difference.

Heat test.—*See* Abel's stability test.

Firing proof for velocity and pressure in a gun of the standard type for the particular form of cordite (*see* Ballistics of a Propellant).

Properties.—Cordite varies in colour from light to dark brown, according to the colour of the mineral jelly used. Cordite Mark I. has the consistency of hard indiarubber. It is somewhat elastic, and can be readily cut with a knife. Cordite M. D. is considerably harder, being more like horn and more brittle, and can only be cut with difficulty.

Cordite has a slight odour of acetone, and it is poisonous. It is water repellant, and can be kept under water, salt or fresh, for some time without its explosive properties being affected. Even when fired wet from a gun, the ballistics only fall off to the extent due to the evaporation of the water. On prolonged cold storage, the nitroglycerin exudes slightly, but is gradually reabsorbed when the temperature rises. The sp.gr. of cordite Mark I. is about 1·56–1·57, that of cordite M. D. being 1·58–1·59.

Cordite does not ignite very readily, but when once ignited it burns slowly with a strong yellowish flame, which is practically smokeless. A stick becomes pointed at the end as it burns, and the flame can be extinguished by blowing strongly on it. A considerable bulk of cordite can be burned away in the open without any explosion. It only burns explosively when strongly confined; if an ignition of the cordite confined in a wooden box takes place, the cordite does not explode, but burns quietly, and the box is only broken open to allow the gases to escape.

Owing to the difficulty of ignition of cordite, a stronger cap of different composition is necessary to ignite the fine cordite in small-arm ammunition than was required for black powder, and to ensure the ignition of the larger sizes the charge of cordite has to be primed with an ordinary black powder or guncotton 'primer,' which passes on the flame of the igniting 'tube' to the charge.

Cordite is very insensitive to shock, and cannot be exploded by the passage of a rifle bullet through it.

Exhaustive trials under very varied climatic conditions have proved that the ballistic stability of cordite is very great.

The ballistic power of cordite is very nearly four times that of black powder, owing to the increased volume of gases liberated per unit of weight and the high temperature of the explosion. It can give a pressure, on explosion, of more than 120 tons per square inch, compared with 43 tons, the maximum obtainable with black powder, but in practice the pressure in a gun does not nearly attain this figure (not above 17 tons per square inch) owing to the relatively large size of the gun chamber compared with the volume of the cordite.

The ballistic results of cordite are more influenced by temperature than was the case with black powder, the pressure developed and velocity of the shot being greater with increased temperature, but not to the extent of seriously modifying the shooting under Service conditions. The smaller the size of cordite, the more rapid the explosion, and cordite burns more quickly under high than under low pressures.

The pressure due to cordite is more gradually developed in the gun than was the case with black powder, and is better sustained. The heat of combustion, products of explosion, and other explosion constants for Mark I. cordite were examined, in 1893, by Deering at Woolwich. He worked with an explosion bomb, made of gun-steel, about 1·27 inches in thickness and 108 c.c. capacity. The following are some of the results obtained with a cordite of the composition: loss, 0·24 p.c.; nitroglycerin, 58·55 p.c.; guncotton, 36·11 p.c.; and mineral jelly, 5·10 p.c.; the figures quoted being the averages of a large number of experiments :—

Pressure developed, tons per sq. inch (by crusher gauge)	6·4	13	16
Vol. of perm gases at 0 and 760 mm., c.c. per gm. cordite	663·7	669·8	671·1
Volume of total ditto ditto	880·7	870·7	869·8
Water formed, gram per gram cordite	0·1757	0·1623	0·1599
Quantity of heat developed, gram degrees C. per gram cordite. water, liquid .	1225	1239·1	1242·9
Ditto ditto. water, gaseous	1131	1152·2	1157·2
P.c.comp.perm.gases, vols CO_2	25·40	-	28·20
CO	37·62		33·82
H	17·43	—	18·55
N	19·55		19·09
CH_4	not dtd		0·34

With the explosion gases at 6·4 tons pressure, Deering calculated the specific heat to be about 0·403, and the temperature of the gases about 2830° ; and with a pressure of 7·0 tons, a specific heat of about 0·366 and a temperature of 3120°. The explosion constants of cordite Mark I. and cordite M. D. have also been determined by Robertson, at Waltham Abbey. The following results were obtained with a density of loading of 0·2 :—

	Cordite Mark I.	Cordite M. D
Heat of explosion, calories per gram, at constant vol. : water, gaseous .	1156	965
Total gases, c.c. per gram, at 0° at 760 mm. : water, gaseous . .	871	920
Temperature of explosion, °C. .	2663	2374

The larger volume of gaseous products and lower temperature explain why the erosive effect of cordite M. D. is so much less than that of cordite Mark I. The experiments of Nobel have already been referred to.

The erosive effects of cordite are less than those of black powder, and of a different character. With black powder, the surface of the gun is pitted by the corrosive action of the products of combustion, whilst with cordite the surface is smoothly washed away, only near the gun chamber, by the passage of the hot gases between the projectile and the bore, before the inertia of the projectile is overcome. Cordite M.·D. gives far less flame than cordite Mark I. when used in rifles or machine guns.

Maxim's powder contains both soluble and insoluble nitrocellulose, mainly insoluble, nitroglycerin, castor oil, and originally an alkaline carbonate. Acetone is the solvent used for gelatinisation. It is made in cylindrical grains or in cords of various diameters.

Axite, made by Kynochs, Ltd., is a guncotton-nitroglycerin powder with vaseline and olive oil, and sometimes potassium and barium nitrates and oxalates, to reduce the temperature of explosion and decrease metallic fouling, made in the form of a rail-shaped ribbon. Its ballistics are equal to those of cordite, and are said to be less variable with changes of temperature.

Moddite, a sporting rifle powder manufactured by Eley Bros., is a gelatinised mixture of nitrocotton, of which one-third is soluble nitrocellulose, and nitroglycerin with about 4 p.c. mineral jelly.

Solenite is an Italian powder used instead of ballistite for guns of large calibre, containing 40 p.c. insoluble nitrocellulose, 30 p.c. soluble nitrocellulose, and 30 p.c. nitroglycerin gelatinised with acetone. It is stabilised with 1–3 p.c. mineral jelly, and is in the form of short tubes.

(4) *Nitrocellulose-Nitro- Derivative Powders.*

Indurite, patented by Munro of the United States (Eng. Pat. 580, 1893), contains 40 p.c. guncotton, freed from lower nitrates by thorough extraction with methyl alcohol, and 60 p.c. mononitrobenzene, with or without oxidising salts. The mixture is rolled into sheets and cut into grains. The grains are treated with hot water or steam, which hardens or indurates them to the consistency of bone : hence the name.

Du Pont powder, patented by Du Pont of the United States (Eng. Pat. 15865, 1893), contains nitrocellulose and nitrobenzene, and sometimes potassium nitrate. The nitrocellulose is agitated in water, the nitrobenzene added, and the mass agitated until the nitrocellulose is dissolved and grains are formed, when the grains are hardened by blowing in steam. In some of the powders, a little nitroresin or nitroturpentine was added as a moderant. Later Du Pont powders contained about 40 p.c. soluble nitrocellulose, 40 p.c. nitroglycerin, and 20 p.c. ammonium picrate, the cylindrical grains being graphited.

Colt's pistol ammunition contains a powder in the form of thin graphited squares, 1 mm. side, consisting of guncotton with about 5 p.c. of dinitrobenzene.

Felixite is a fibrous, 42-grain, bulk powder, manufactured by the New Explosives Co. at Stowmarket, containing both metallic nitrates and nitrohydrocarbon, and about 3 p.c. vaseline. *Red star* and *N. E. powder* are powders of different grade, the former 33 grain, the latter 36 grain, containing the same ingredients in different proportions.

Greener's powder is a nitrocellulose-nitrobenzene powder coloured with lampblack.

Rifleite, manufactured by the Smokeless Powder Co. of Warwick, is a nitrocellulose powder gelatinised by acetone containing a small proportion of dinitrotoluene, and the *S.S. powder*, smokeless shot-gun, of the same company is a similar powder containing a rather large proportion of barium nitrate with a little potassium nitrate and a little wood meal. *S.R.*, a sporting rifle variety of this powder, is thoroughly colloided. It contains mainly soluble, instead of insoluble nitrocellulose, a higher proportion of nitrohydrocarbon, about 20 p.c. metallic nitrates, and 8 p.c. starch. It was introduced in 1890, and was the first practical colloidal smokeless powder considered for military purposes.

Kynoch's smokeless powder is similar in composition to S.S. powder.

Plastomenite is a German powder invented by Güttler, made by incorporating one part of nitrolignin with 5 parts of fused dinitrotoluene and granulating the fused mass. It may also contain barium nitrate.

Some forms of *Norwegian ballistite* contain from 5 to 6 p.c. nitronaphthalene.

Ruby powder is a fibrous, 42-grain, bulk sporting powder, manufactured by Curtis's and Harvey, containing about 50 p.c. nitrocellulose, mainly insoluble, with metallic nitrates, about 8 p.c. nitrohydrocarbon, and 6 p.c. starch.

Smokeless powders containing picrates, usually ammonium picrate, have been frequently tried, both for sporting and military purposes, but they have been practically abandoned at the present time. A recently suggested propellant for small arms and guns by the Powderite Explosives Co., of New South Wales (Eng. Pat. 16505, 1915), is a nitroglycerin powder with 1 p.c. mineral jelly, and 2 p.c. calcium picrate. It is claimed to be more powerful than cordite, and quite stable. Some of the early French military smokeless powders contained picric acid, and at one time a powder containing about 5 p.c. ammonium picrate was tried in the Mauser rifle by Germany.

The American *Peyton powder* was, at one time, a nitrocellulose and nitroglycerin powder containing about 20 p.c. ammonium picrate.

FULMINATES.

Although the fulminates of many heavy metals have been prepared, most of them are exceedingly sensitive and too unstable for use in explosives. The mercury salt is the only one in practical use, though *silver fulminate* has been licensed for use in toy fireworks only. Silver fulminate is prepared in a similar manner to mercury fulminate. It is more sensitive to friction and percussion than the mercury compound, and has a greater explosive power.

Mercury fulminate, discovered by Howard in 1800, is produced by the reaction which ensues on mixing together alcohol and a solution of mercury in excess of nitric acid.

In Liebig's process, and Chevalier's modification of it as used in France, the solution of mercury in nitric acid is used cold; in Chandelon's process it is used warm.

Chevalier's process. 3 parts by weight of mercury (300 grams) are dissolved in the cold in 30 parts of nitric acid of 1·34 sp gr., and the solution is poured into a flask containing 19 parts of alcohol (of 90 p.c strength). After some minutes an energetic reaction commences, with formation of crystals of mercury fulminate. Towards the end of the operation two successive additions of 2·38 and 1·58 parts of alcohol are made; the fulminate obtained is thoroughly washed and dried.

The addition of too large a quantity of cold alcohol towards the end of the operation is stated to yield an impure fulminate. The yield by this process varies between 118 and 128 p.c. of the weight of mercury used.

Chandelon's process is the one almost universally used, and the original proportions are usually closely adhered to. 1 part by weight of mercury is dissolved in 10 parts of nitric acid (sp.gr. 1·4) at a gentle heat; the solution, at a temperature of about 55°, is poured into a capacious flask or retort (its capacity must be at least equal to six times the volume of the liquid) containing 8·3 parts of alcohol (of sp.gr. 0·83). The flask is connected by a cork and tube with a stoneware condenser, to recover spirit.

In about a quarter of an hour, the reaction commences with a slight formation of gas bubbles; very soon the liquid boils, and the flask becomes filled with voluminous white vapour. The violence of the action can be checked by adding, as required, a little alcohol; for this purpose the recovered spirit after redistillation with caustic soda can be utilised. If the reaction be too much restrained in this way, the fulminate is likely to contain metallic mercury.

The mercury fulminate is precipitated from the liquid in small greyish-coloured needles. When the action is over, the contents of the retort are cooled down quickly and the mother liquid poured off, the fulminate is filtered and washed, then passed through a fine net filter to remove large crystals, and finally washed on a finer net filter until free from acidity. The nitric acid liquid, after cooling, does not contain any appreciable quantity of mercury. The calculated yield of fulminate is 142 per 100 of mercury; by this process the mean yield is 125 p.c. mercury fulminate.

A process very similar to the above is employed in this country; the yield of fulminate is about 123 parts per 100 of mercury.

Mercury fulminate is usually light brown-grey in colour. *White fulminate* of mercury is manufactured by adding a little copper and hydrochloric acid or potassium chloride to the solution of mercury nitrate, before pouring it into the alcohol. Solonina (Zeitsch. Ges. Schiess- u. Sprengstoffwesen, 1910, 41, 67) finds that other chlorides have a similar effect, but that the use of hydrochloric acid alone leads to the formation of a considerable quantity of oxalic acid which contaminates the fulminate. He finds that the purest fulminate results from the addition of cuprous chloride.

Mercury fulminate is sometimes recrystallised from boiling water or from alcohol, but this is not usually found necessary. The best method of purification is to dissolve in pyridine, filter the solution, and precipitate by adding an excess of water. Traces of free mercury can be removed from fulminate by placing it for a few days in a vacuum desiccator.

Angelico (Chem. Zentr. 1901, ii. 404) prepares mercury fulminate by treating a solution of mercury in an excess of dilute nitric acid with a strong aqueous solution of malonic acid and a little sodium nitrite solution. A considerable rise of temperature takes place, with copious evolution of carbonic acid gas, and crystals of fulminate separate out. So far as is known, this process has not been used on the manufacturing scale.

Fulminate is usually stored in linen bags immersed in water. The explosive power of samples is unaffected even by prolonged storage under these conditions at normal temperatures. Before use it is usually washed through a 40-mesh sieve. If dry fulminate is required, it is spread out on linen or paper, supported in wooden frames with string-net bottoms, and dried in a current of dry air, or it is spread out on cloths on copper tables, varnished with copal to prevent attack by the wet fulminate, heated either by hot water or steam, at a temperature of about 40°, the temperature not being allowed to rise above 45°. Passburg of Breslau has devised an apparatus for drying fulminate of mercury in a vacuum. The drying chamber is heated by steam, which can be replaced by cold water when the fulminate is dry. Explosives only burn with difficulty in a vacuum, and there is sufficient vacuous space, with the aid of safety valves, to prevent any damage, should an ignition take place of the quantity of fulminate dried at one time. When dry, the fulminate is allowed to cool, any lumps are broken down by a soft pad, and the fulminate passed through a muslin cloth. The dry fulminate is stored in papier mache cylinders with lids.

Properties.—Commercial mercury fulminate is in the form of small crystals, of white or pale-brown colour. The crystals of most commercial samples all pass an 80-mesh sieve, 80 p.c. or so pass a 120-mesh, and about 60 p.c. pass a 200-mesh. Some very fine crystal dust is usually present. It crystallises in well defined octahedra, which frequently twin along the major axis, and repeated twinning to form ladder like crystals is common. The larger crystals are usually truncated to such an extent that they form plates.

In a state of purity it crystallises in white silky needles. It is almost insoluble in cold water, but soluble in 130 times its weight of boiling water. It is decomposed slowly by boiling water, and even at lower temperatures on prolonged digestion. The brown colour of some commercial samples, attributed to the presence of resinous impurities, is usually evenly distributed throughout the crystals, but in some samples it occurs mainly along the edges of the crystals, or in spots. The larger crystals generally have the darker colour. It is soluble in pyridine and alcohol. Fulminate may be dissolved to a clear solution in ammonia, and in solutions of potassium cyanide or sodium thiosulphate. The primary reaction for the solution in thiosulphate is represented by the equation

$$Hg(CNO)_2 + 2Na_2S_2O_3 + 2H_2O = HgS_4O_6 + C_2N_2 + 4NaOH$$

A small residue is left from commercial samples, which consists largely of free mercury, but also contains mercury compounds, containing carbon and hydrogen, of uncertain composition. It has a sweetish metallic taste, and is usually stated to be very poisonous. However, fungi frequently grow on organic matter, the linen bags and wooden barrels in which fulminate is stored, in contact with its dilute solution in water, and workmen engaged in handling wet fulminate do not show signs of mercury poisoning. A non-poisonous property would accord more with the fact that an aqueous solution of fulminate does not give the ordinary reactions for mercury ions.

Its sp.gr. is 4·42 (Berthelot and Vieille). The bulk density of different samples varies considerably, and mainly according to the size of the crystals. It is difficult to get very concordant results, as much depends on the amount of tapping, but comparative figures for fine and coarse fulminates were 1·35 and 1·55 respectively. This variation is of importance in charging fulminate detonators by measurement. In the dry state it explodes violently by a moderate blow or by slight friction; its sensitiveness is lessened when it is moistened with water. Large crystals and complex crystals and clusters are more sensitive than small crystals. Thus Berthelot states that the presence of 30 p.c. of water prevents the decomposition of the fulminate in fine powder by friction or shock, that with 10 p.c. of water it decomposes without detonation, that with 5 p.c. water only the portion struck detonates. These results were, however, obtained with small quantities of fulminate, and should not be presumed on in manipulating the substance. In small quantities it will burn fiercely without explosion when ignited, and large quantities may be safely destroyed by burning it in a train after mixing with oil. Mercury fulminate, when heated with a large volume of water under pressure, decomposes into metallic mercury and non-explosive mercury compounds of unknown composition. Small quantities may be destroyed by warming with ammonium sulphide or sodium thiosulphate, care being taken that the sulphide or thiosulphate is in sufficient excess.

When only slightly confined, even between sheets of paper, mercury fulminate explodes violently when ignited.

It is detonated by heat; the temperature of explosion is variously stated as 187°, 200°, and 149°. The firing-point, as usual, depends on the form of apparatus and the rapidity of heating up; ignition takes place at a lower temperature if the explosive be slowly heated than when heating up is rapid, and with increased quantity of material, when this is small, up to a limiting weight. The results are, no doubt, influenced by the heat of decomposition of the material decomposing before ignition. Wöhler found that with 0·02 gram of fulminate detonation took place after 5 seconds at a temperature of 215°.

It can also be exploded by a spark from an induction coil or by contact with strong sulphuric acid. Fulminate can be exploded by contact with a wire heated to incandescence by means of an electric current, but *in vacuô* only the part actually in contact fires.

The products of its detonation are carbonic oxide, nitrogen, and metallic mercury. Berthelot and Vieille examined them—the fulminate being detonated in an atmosphere of nitrogen—and obtained in five experiments per 1 gram fulminate 234·2 c.c. of gases, consisting of CO_2 0·15 vol., CO 65·70 vols., N 32·26 vols., H 1·89 vols. per 100 vols. gas. This agrees with

$$HgC_2N_2O_2 = 2CO + 2N + Hg$$

requiring 235·6 c.c. From these results and from an estimation of the mercury, they obtain for the composition by weight of mercury fulminate, C 8·35 p.c., Hg 71·30 p.c., N 9·60 p.c., O 11·05 p.c., H 0·04 p.c., total 100·34, every constituent having been estimated. This confirms the accepted formula $HgC_2N_2O_2$, requiring C 8·45 p.c., Hg 70·42 p.c., N 9·86 p.c., O 11·27 p.c. The fulminate analysed contained a trace of metallic mercury.

The decomposition $HgC_2N_2O_2$ into

$$2CO + 2N + Hg$$

disengages +114·5 Calories (kgm.-degrees) of heat at constant pressure per 284 grams fulminate, the mercury supposed liquid; for mercury gaseous, +99·1 Cals.; or per 1 kgm. fulminate, 403 Cals. and 349 Cals. respectively. Mercury fulminate is an endothermic substance; in its formation from its elements there is absorption of heat, −62·9 Cals. per 284 grams, or −221·5 Cals. per 1 kgm.

The pressure produced by the detonation of cury fulminate in a space entirely filled t has been estimated by Berthelot and Vieille he crusher-gauge apparatus of the former; find it to be more than twice that of nitro-erin, and about three times that of gun-on, detonated in spaces filled by them (but ding the interstitial air of the guncotton). attribute the power of mercury fulminate ffecting detonation to the greatness of this ure, coupled with its sudden development thelot and Vieille, Annalen, [21] 569, 1880).

The main factor causing the detonative racter of the explosion of mercury fulminate, perhaps, the extreme rapidity of the explo-n, which is further helped by the high density the explosive. The effects of the detonation fulminate and fulminate compositions are ways quite local. The sharpness of the plosion is also no doubt connected with the ct that the products of detonation do not dergo dissociation, and so the explosive re-tion is not prolonged by this phenomenon, as usually the case

The larger the crystals of fulminate, the more sily can it be detonated and the greater the plosive effect: for this reason, brown or grey lminate is slightly more powerful than white.

Testing: Microscope.—The crystals should well defined, of uniform size, and free from sible impurities. Metallic mercury can some-nes be detected.

Total mercury is estimated by dissolving the mple in strong ammonia or a solution of tassium cyanide, precipitating with am-onium sulphide, and weighing the mercury lphide as usual. It may also be estimated by ectrolytic deposition on copper. The sample ould preferably be dried in an atmosphere turated with mercury vapour to prevent loss free mercury. Commercial samples generally ntain about 70 5 p.c. Hg.

Fulminate is determined by the method described by Philip (Zeitsch. Ges. Schiess- u. Sprengstoffwesen, 1912, 180, &c.) 0·3 gram of the fulminate is dissolved in 50 c.c. N/10-thiosulphate containing 3 grams of potassium iodide. The following reactions take place:

$$\mathrm{Hg(ONC)_2+4KI=K_2HgI_4+2KONC}$$

$$\mathrm{2KONC+2H_2O=2HONC+2KOH}$$

$$\mathrm{2HONC+H_2O+2Na_2S_2O_3}$$
$$\mathrm{=Na_2S_4O_6+2NaOH+HCN+HCNO}$$

The free alkali is determined by N/10 sulphuric acid, and the excess of thio- may also be determined by titration with N/10 iodine solution and starch. Pure fulminate should give identical results by the two titrations. Supplies give from 98·5 to 99·5 p.c. mercury fulminate by this method of estimation.

Free mercury is determined by dissolving the sample in 0·880 ammonia or other solvent, filtering and washing the residue, and determining the mercury in it as usual. As already mentioned, this residue also contains some mercury compounds; an idea of the quantity of free mercury can be got by examining the residue on the paper microscopically before dissolving in acid.

Oxalate is determined in the filtrate from the mercury sulphide in the total mercury estimation, by adding NH_4Cl and $CaCl_2$.

Carbon and nitrogen may be estimated by a careful combustion, if the fulminate is mixed with a large excess of copper oxide. The mercury is absorbed by gold leaf placed in the calcium chloride tube.

Explosive power is found by firing in lead blocks. 20 grains are fired, electrically, in a cylindrical lead block 6 inches high and 4 inches in diameter, with an axial cylindrical hole 0·25 inch in diameter and 3 inches deep. The enlargement of the cavity formed, measured by running in water from a burette, is an index of the explosive power, as compared with that of standard samples.

Fulminate Compositions.

Mercury fulminate is used in detonators, and is the active ingredient in igniting and detonating mixtures, its value depending on its extreme sensitiveness to friction and percussion.

Igniting mixtures. Mercury fulminate is too rapid in its action to be used alone. On firing a train of fulminate covered with gunpowder or cordite, the latter are simply dispersed without being ignited. If the fulminate be mixed with a little potassium chlorate, the rate of burning is decreased, and the temperature and flame increased by the combustion of the carbonic oxide, and the powders are ignited. The explosion with potassium chlorate may be represented by:

$$\mathrm{3HgC_2N_2O_2+2KClO_3=2KCl+3Hg+6CO_2+3N_2}$$

A mixture of 22·3 p.c. potassium chlorate and 77·7 p.c. mercury fulminate, *i.e.* in the proportion required for the oxidation of the carbon to carbon dioxide, gives by its explosion 706 cals. (mercury, liquid) or 663 cals. (mercury, gaseous) per 1 kgm of mixture. The volume of gases (at 0° and 760 mm.) produced is 183 litres per 1 kgm.—less than with the fulminate alone; the theoretical pressure is very near that of pure fulminate. The chlorate renders the mixture very sensitive (Berthelot).

Percussion caps were invented by Egg in 1815, Forsyth having suggested the percussion system of ignition in 1807. The cap shells are small closed cylinders usually of pure copper. In the early caps, pure fulminate was used agglomerated by means of wax or an aqueous solution of gum.

In later igniting compositions, mercury fulminate and potassium chlorate were mixed with other combustible substances, such as antimony sulphide, sulphur, and mealed powder, to increase the size of the flame and ensure ignition of the powder. Powdered glass is frequently added to increase the frictional surfaces and sensitiveness of the composition. The best igniting composition for any particular composition and form of propellant has largely to be found by experiment.

A cap composition must not be too slow nor too rapid in its rate of burning. If too slow, much of the heat of combustion may be conveyed to the metal parts and irregular ignition of the propellant or even miss-fires may occur; and, on the other hand, if too rapid the charge of propellant is disturbed and uneven ignition and irregular firing results are obtained. There should be a certain proportion of solid ingredients of high specific heat in the combustion products, in order to make ignition certain. To secure regularity of ignition, the ingredients of the composition should be of even size and well mixed.

Aluminium powder has been suggested by Brownsdon (Eng. Pat. 23366, 1904) as an addition to increase the strength of cap composition, the metal being either mixed with the other ingredients or pressed in a layer on the surface. Zieger (Eng. Pat. 14583, 1900) suggests barium nitrate, with a little barium carbonate, as a substitute for the potassium chlorate: the products are said to act less corrosively on the gun-barrel, and the carbonate is said to give stability to the mixture.

For black gunpowder, the English Service cap composition was a mixture of 37·5 p.c. mercury fulminate, 37·5 p.c. potassium chlorate, and 25 p.c. antimony sulphide, with in some cases 12·5 p.c. ground glass, the charge being 0·22 to 0·25 grain per cap. A mixture of similar composition was used by most other countries.

For smokeless powders, which are more difficult of ignition, a slower mixture with a longer flame is necessary. The Service composition for cordite small-arm ammunition is composed of 19·05 p.c. mercury fulminate, 33·33 p.c. potassium chlorate, 42·86 p.c. antimony sulphide, and 2·38 p.c. each sulphur and mealed powder. The charge per cap is 0·6 grain. Barium nitrate now replaces a large proportion of the potassium chlorate in many commercial cap compositions, a suitable composition being 40 p.c. mercury fulminate, 39 p.c. barium nitrate, 7 p.c. potassium chlorate, and 14 p.c. antimony sulphide. The ingredients, other than fulminate, are usually ground so that they pass a 120-mesh sieve, but it is desirable also that they should not contain much dust, or the sensitiveness of the composition may be seriously lowered. The presence of grit, such as is frequently present in commercial samples of antimony sulphide, has a marked effect in increasing the sensitiveness of these compositions.

Mixing cap compositions.—The ingredients of cap compositions were formerly mixed in a wooden mortar for some hours, after wetting with an aqueous solution of gum arabic or an alcoholic solution of gum benzoin, or were mixed by hand on paper and afterwards sifted. The ingredients are now usually mixed dry. In England and France, a so-called 'jelly bag' is used; this is a conical silk bag with rows of indiarubber rings strung on cords passing from top to bottom. The contents are mixed together by working the bag up and down by means of a cord fastened to the apex of the bag. The mixing only takes a few minutes. In Germany, a similar principle is used, but the mixer is saucer-shaped and contains indiarubber balls.

Charging the caps.—At one time the caps were charged with the wet composition by hand, but now the charging is always done by a machine. The composition in the cap shells is compressed by a pressure of about 1000 lbs. per square inch, and then covered with shellac varnish or a tinfoil disc, or sometimes both.

Proof.—The usual proof of caps comprises the microscopic and analytical examination of the composition, photographing the flash, detonating in a cavity in a lead bar and measuring the enlargement of the cavity and noting the comminution of the cap shell, and a firing proof when made up into cartridges. In special examinations, determinations are made of the total heat of combustion, temperature, and duration of the flash, the volume of gaseous products and their relation to the solid product of combustion, &c. (For details, *see* papers by Brownsdon, J. Soc. Chem. Ind. 1905, 381; and Borland, *ibid.* 1906, 241.)

Detonators may be fired electrically or by the flame from a fuse, and the construction varies accordingly, but the detonating composition is contained in what are practically long percussion caps made generally of copper.

The charge, as in the case of caps, was at one time pure fulminate, and is at the present time in many Service detonators, but a mixture of fulminate with potassium chlorate, and sometimes other ingredients, such as guncotton, is now usually used in industrial detonators. The mixtures contain 80 to 90 p.c. mercury fulminate; 80 p.c. fulminate is common in England, 90 p.c. in the United States.

Hagen (Zeitsch. Ges. Schiess- u. Sprengstoffwesen, 1912, 201, &c.) states that the addition of potassium chlorate increases the detonative efficiency of mercury fulminate, owing to the increased heat and gas pressure produced; but Wöhler (Zeitsch. angew. Chem. 1911, 209) is of the opinion that the increase of total energy resulting from the addition of the chlorate is more than counterbalanced by the decrease in the velocity of detonation. Storm and Cope (U.S. Bureau of Mines, Tech Paper 125, 1916), by practical experiments in their sand bomb apparatus, found that 80 : 20 fulminate-chlorate mixture had greater detonative power than the 90 : 10 mixture, and that the latter in turn is superior to mercury fulminate alone. For example, for complete detonation of 0·4 gram of 'tetryl,' 0·35 gram of mercury fulminate, 0·30 gram of 90 : 10, or 0·275 gram of 80 : 20, fulminate-chlorate mixture is required. If the detonating composition be compressed very highly in detonators it simply burns on contact with flame, but within the limits of compression used in commercial detonators the degree of compression has little or no effect on the detonative power. The presence of 0·75 p.c. moisture in the charge of a detonator filled with 90 : 10 composition was found to have practically no effect on its detonating efficiency. Tests by Taylor and Cope (U.S. Bureau of Mines, Tech. Paper 162, 1917), carried out with mixtures of mercury fulminate with various oxygen carriers, did not show any relationship between the priming efficiency of the mixtures and any property of the oxidising salt; they all gave equally efficient mixtures. They found mercury fulminate to be more efficient as a detonating agent when uncompressed than when compressed, whereas the efficiency of detonators containing lead azide increased with the loading pressure. They conclude that the detonating efficiency of an explosive depends on two factors, an intensity or quickness factor, depending on the acceleration of the explosive reaction, and a capacity factor, the 'strength' of the explosive, as measured by the sand bomb apparatus, the intensity factor being the more important. Silver acetylide has low detonating power, but increases the efficiency of mercury fulminate, probably due to the low 'strength' but great 'quickness' of its explosion.

The property of detonating another explosive does not depend merely on the violence of an explosive, for Abel found that 0·32 gram of mercury fulminate would detonate guncotton, whereas ten times the weight of the more violent nitrogen chloride was required. To explain the value of an explosive in initiating detonation in other explosives, Abel (Compt. rend. 1874, 1228) advanced his theory of wave synchronism or sympathetic vibration. Wöhler and Matter (Zeitsch. Ges. Schiess- u. Sprengstoffwesen, 1907, 181, &c.), in the case of mercury fulminate, attributed its value as a detonant to the pressure produced by the kinetic energy of the molecules, that is, that it is due primarily to the rate of detonation and density of the fulminate, and secondarily to the gas volume and heat evolved. Nobel attributed this property of fulminate to the very intense shock or pressure instantaneously set up on its explosion, and Berthelot, as mentioned when considering the properties of mercury fulminate, adopted the same view, but also called attention to the contributing fact that the products of explosion undergo little, if any, dissociation. It is certain that velocity of detonation and power, or total energy, alone do not determine the value of an explosive as a detonant, otherwise nitroglycerin and blasting gelatin would have greater, instead of far less, detonating value than mercury fulminate, and mercury fulminate would have greater value than its admixtures with an oxidising salt. It is probable that all these factors are contributory to the property of initiating detonation, and considering the high value of this property of silver, mercury, and lead compounds, fulminates, azides, picrates, and acetylides, it still seems that Abel's original theory, or something analogous to it, is not entirely to be neglected.

The detonators are charged and the charge compressed as with caps, except that detonators are usually compressed singly, owing to the strength of the charge. A pressure of about 4000 lbs. per square inch is used, giving the fulminate or mixture a density of 2·8. The ingredients should be even in size and well mixed to act efficiently.

The following detonators are used :—

Description No.	1	2	3	4	5	6	7	8
Charge, grams .	0·3	0·4	0·54	0·65	0·8	1·0	1·5	2

They vary in length, from 16 to 45 mm., and in diameter from 5·5 to 6·8 mm.

To obtain the full effect from a detonating explosive, a detonator of sufficient power is necessary. A No. 3 detonator is sufficient for ordinary dynamite, but for the modern safety explosives, such as those of the ammonium nitrate class, at least a No. 6 detonator is necessary for effective detonation of the explosive.

As a detonating composition for high explosives, which can be fired with safety in shells, Maxim (Eng. Pat. 18682, 1894) proposes a mixture of 75 to 85 p.c. of mercury fulminate with 15 to 25 p.c. of a blasting gelatin composed of 75 to 85 p.c. of nitroglycerin and 15–25 p.c. of collodion cotton. The admixture is aided by the use of acetone, and to decrease the sensitiveness the mixture is sometimes made of a spongy nature by blowing air through it whilst it is in a syrupy condition, or nitrobenzene may be added.

Other igniting and detonating compositions. Many mixtures, frequently not containing mercury fulminate, have been from time to time suggested. The drawback to fulminate cap compositions is that the mercury in the combustion products attacks the metal of the cartridge cases, causing them to crack and be unfit for further recharging. Early mixtures containing guncotton and potassium chlorate, lead picrate, &c., were not very successful. Mixtures of mercury or lead thiocyanate with potassium chlorate, and of mercury or lead chromate, mercury fulminate, antimony sulphide, and powdered glass have been proved efficient with certain sporting powders. A mixture of 82·8 p.c. of mercury fulminate and 17·2 p.c. of ammonium perchlorate was suggested by Alvisi (U.S. Pat. 707493, 1902). It was proposed by Bielefeldt (Eng. Pat. 20133, 1900) to substitute all or part of the mercury fulminate in detonating composition by picric acid, nitronaphthalene, nitrocellulose, &c. With safety explosives, he also suggested the addition of aluminium nitrate. Wöhler (Eng. Pat. 21065, 1900) proposed the use of high nitro derivatives, such as trinitrotoluene; and Gehre (Eng. Pat. 19402, 1905) suggested di- or tri-nitromesitylene, and di- or tri-nitropseudocumene. A little fulminate is necessary to ensure detonation, but with trinitrotoluene not more than one-tenth of the usual quantity. Trinitrotoluene detonators are very largely used in Germany, and the Rheinsch-Westfälische Gesellschaft have patented the use of tetranitromethylaniline, or 'Tetryl' (Eng. Pat. 13340, 1905). Swope (U.S. Pat. 1194095, 1916) suggests a compressed mixture of nitrocellulose, or other nitrocarbohydrate, a thiocyanate, and a chlorate as a priming or detonating composition.

As substitutes for mercury fulminate, Angeli (Fr. Pat. 327892, 1902) proposed the barium, strontium, or calcium salts of the hydroxamic acids; Wöhler (Ger. Pat. 196824, 1907) proposed the azides of silver, mercury, or other heavy metal; it is claimed that a smaller quantity of these substances is necessary. Hyronimus (Eng. Pat. 1819, 1908) suggested the use of lead azide. The azides are coming into increasing use for igniting and detonating compositions. The Winchester Repeating Arms Co. (U.S. Pat. 1174669, 1916) suggest a mixture of lead azide, a nitro compound, such as nitrocellulose, and a substance such as an alkaline azide, which leaves an alkaline residue on ignition; and Buell (U.S. Pat. 1184316, 1916) suggests sodium azide, with or without potassium chlorate, and antimony sulphide as an igniting charge. Herz proposed nitrodiazobenzene perchlorate (Fr. Pat. 450897, 1913), and Von Girsewald (J. Soc. Chem. Ind. 1912, 1068) suggested hexamethylenetriperoxidediamine as detonating agents. They both have great efficiency, being decidedly superior to mercury fulminate or lead azide, but they are gradually and progressively decomposed by the moisture in the atmosphere on storage. Buckard (Eng.

Pat. 16405, 1914) suggests their use in composite detonators, in which these substances are primed and further protected by an igniting charge of cap composition. The tetranitrate of pentaerythritol is suggested by Stettbacher (Zeitsch. Gess. Schiess- u. Sprengstoffwesen, 1916, 11) as suitable for use in primers and detonators.

Mixtures, without fulminate, containing aluminium, have been proposed by Führer (Eng. Pat. 2755, 1901, and 24812, 1902), Bielefeldt (Eng. Pat. 7148, 1901), and von Dahmen (U.S. Pat. 702357, 1902), but these mixtures require very strong confinement to be effective; the Westfälisch - Anhaltische Sprengstoff Actien-Gesellschaft have patented mixtures without fulminate, containing potassium chlorate with mono-, di-, or tri-nitrocresol, &c.; and Bielefeldt (Eng. Pat. 23889, 1901) suggests a mixture of potassium chlorate with trinitronaphthalene.

Composite detonators, in which the main base charge is tetryl, trinitrotoluene, or other nitro- body or organic nitrate, primed by mercury fulminate, a fulminate-chlorate mixture, or lead azide, are now used very largely instead of a heavy charge of mercury fulminate For example, a base charge of 0·32 gram of tetryl primed with about 0·32 gram of a 9 to 1 fulminate-chlorate mixture will make a detonator of about No. 6 power, and so effect considerable saving of the expensive mercury fulminate. In *reinforced detonators* an inner perforated metal shell is pressed down over the charge.

Efficiency.—Detonants have, by their effect when detonated on a lead plate, been placed in the following order of efficiency as regards their value as initial detonants for other explosives, by Wöhler and Mauer (Zeitsch. Ges. Schiess- u. Sprengstoffwesen, 1907, 265): silver azoimide, mercury fulminate, trimercuraldehyde and a perchlorate, trimercuraldehyde and a chlorate, diazobenzene nitrate, nitrogen sulphide, sodium fulminate, and mercury nitromethane. Wöhler and Matter (Zeitsch. Ges. Schiess- u. Sprengstoffwesen, 1907, 245) found that the detonative power of a detonating charge depends on the conditions of use, especially on the area of contact surface between the detonator and the explosive. By trial with a No. 8 detonator, the 2-gram charge of which was compressed at pressures from 100 to 2000 kgms. per square cm., they found at first a decrease in the size of the cavity in the lead block test, with increased loading density, but still higher densities of loading give no difference in result.

The sand bomb test (*see* p. 95) is an excellent method for comparing the efficiency of detonators.

OTHER EXPLOSIVE COMPOUNDS.

Nitrostarch. Braconnot and Pelouze first nitrated starch at the same time as cellulose, the explosive product, like nitrocellulose, being originally called 'xyloldin.' Attempts to use nitrostarch, from time to time, for explosive work failed, partly owing to the instability of the product, and partly because, owing to the difficulty in nitration, the product had a considerably smaller nitrogen content than nitrocellulose.

Braconnot and Pelouze carried out the nitration with nitric acid alone. Uchatius first used a mixture of nitric and sulphuric acids. In his process the starch was not added directly to the acid mixture, as it clotted together and resisted nitration, but was dissolved in 8 parts of cooled fuming nitric acid and the syrupy solution poured, with stirring, into 16 parts of concentrated sulphuric acid. The mixture was allowed to stand for 12 hours, washed, boiled with a solution of sodium carbonate, and dried at 60°.

The product was a white powder insoluble in water and alcohol, but soluble in ether. It was very hygroscopic and readily decomposed spontaneously, doubtless because of insufficient purification. It ignited at about 175°, and was very explosive.

Later, in America, Volney succeeded in nitrating starch directly in cold mixed acids by using a special stirring apparatus.

The Actien-Gesellschaft Dynamit Nobel, in 1891, patented the use of nitrostarch in smokeless powders (Eng. Pat. 6129, 1891), and prepared it on the manufacturing scale. The method of preparation is similar to that of Uchatius. The well-dried starch is first dissolved in 10 parts of nitric acid, of 1·5 sp.gr., in a special apparatus of lead, in which the mixture is well circulated by means of a paddle stirrer, and kept well cooled by means of inner and outer water-jackets. When all the starch is dissolved, the solution is introduced as a spray from an 'atomiser' into five times its weight of mixed acids, as a rule waste acids from nitroglycerin manufacture, containing 70 p.c. H_2SO_4, 10 p.c. HNO_3, and 20 p.c. H_2O. The nitrostarch is precipitated as a fine powder, and is retained on a filter of guncotton between two perforated plates, when the waste acids are run off from the bottom of the vessel. The acid is pressed out, and the cake of nitrostarch stirred in water until neutral. The product is treated for 24 hours with a 5 p.c. solution of sodium carbonate, and finally stabilised by soaking in a solution of aniline. The finished cake contains about 23 p.c. water and 1 p.c. aniline. The nitrostarch so obtained is a mixture of mono-, di-, and tetra-nitrates, when related to $C_{12}H_{20}O_{10}$ as the molecule of starch—that is, up to and mainly $C_{12}H_{16}O_6(NO_3)_4$, containing 11·11 p.c. nitrogen. It is readily soluble in nitroglycerin, even in the cold, and forms gelatinous to waxy solids when sufficient of the nitrostarch is added.

The penta- and hexa- nitrostarches, on the same basis, have been prepared by Mühlhäusen (Dingl. poly. J. 1892, 137). *Pentanitrostarch* $C_{12}H_{15}O_5(NO_3)_5$, containing 12·75 p.c. nitrogen, was prepared by adding dry starch to twenty times its weight of a mixture of 1 part of nitric acid, sp.gr. 1·5, and 3 parts of sulphuric acid, sp.gr. 1·8. The product, stabilised in the usual way, was freed from the tetranitrate by dissolving in ether-alcohol and distilling off the ether. The tetranitrate remained in solution in the alcohol, and the pentanitrate was precipitated. *Hexanitrostarch* $C_{12}H_{14}O_4(NO_3)_6$, containing 14·14 p.c. nitrogen, was prepared, mixed with the pentanitrate, by dissolving dry starch in ten times its weight of nitric acid, sp.gr. 1·5, standing 24 hours, and pouring the solution into five times its weight of sulphuric acid, sp.gr. 1·77.

A nitrostarch containing 16·5 p.c. nitrogen, corresponding to an *octonitrate* of the composition $C_{12}H_{12}O_2(NO_3)_8$, was prepared by Hough in the

United States in 1904 (U.S. Pat. 751076, 1904) by injecting dried maize starch below the surface of an acid mixture consisting of 3 parts of strong nitric acid, 2 parts of strong sulphuric acid, and sufficient Nordhausen sulphuric acid, containing 40 p.c. SO_3, to give an excess of 2 to 3 p.c. of unhydrated SO_3. The temperature is kept at 7° to 10°, and Nordhausen acid is added during the nitration to keep up the strength of the mixture. The nitrated starch is filtered off, washed, and treated with hot dilute ammonia to dissolve out lower nitrates and stabilise the product. The final product is an orange-coloured powder, soluble in ether-alcohol. Subsequently, Holmes (U.S. Pat. 779422, 1905) stabilised the product by dissolving in a mixture of alcohol and acetone, and then evaporating off the acetone. The impurities and lower nitrates remain in solution in the alcohol.

This nitrostarch is used in several American smokeless powders, and was also for a time tried as a constituent in a U.S. Service powder.

The production of so highly nitrated a starch as claimed by Hough has been questioned by Berl and Butler (Zeitsch. ges. Schiess- u. Sprengstoffw. 1910, 82). Using Hough's method, they failed to obtain a product with a higher nitrogen content than 13·44 p.c. A stable nitrostarch containing 14 p.c. nitrogen was prepared by Will and Lenze (Ber. 1898, 68) by dissolving dried starch in cold nitric acid of sp.gr. 1·52, standing for 24 hours, and gradually adding sulphuric acid. The product was washed with water, then cold alcohol, and finally hot alcohol, and further purified by dissolving in a mixture of acetone and alcohol, and precipitating by evaporating off the acetone. The ignition-point of the product, 194°, was considerably higher than those of the earlier products of the Nobel Co., and of Hough, which ranged from 120° to 175°.

Properties.—Nitrostarch is a white powder, readily soluble in acetone and ethyl acetate, but all preparations are not soluble in ether-alcohol. It is soluble in nitroglycerin, but does not gelatinise it as collodion cotton does. Berl and Butler (*l.c.*), by comparing the viscosities of the solutions in acetone, showed that the molecular complexity of nitrostarch is very small as compared with that of nitrocellulose, which explains the non-gelatinisation of nitroglycerin. Saposhinkoff (J. Russ. Phys. Chem. Soc. 1903, 126), by boiling-point determinations of solutions in acetone, concluded that the molecular weight of nitrostarch containing 13·4 p.c. nitrogen corresponds to a C_{36} formula.

Besides being more difficult to manufacture and less stable than nitrocellulose, nitrostarch is decidedly more hygroscopic, but its manufacture has been improved, and many suggestions have been made for its use in explosives, especially in the United States. A more stable product, for example, is stated by Sadtler (U.S. Pat. 1211761, 1917) to be obtained by preliminary treatment of the starch with a solution of caustic soda, and then with nascent oxygen, to swell the grains and remove impurities. After nitration, the first stabilisation is carried out, as has been found best with nitrocellulose, by boiling the product in the presence of a small amount of residual acid. Some mixtures that have been suggested are: Pieters (U.S. Pat. 1048578, 1912), a blasting explosive containing 20 p.c. nitrostarch, 75 p.c. ammonium nitrate, 4 p.c. nitrobenzene, and 1 p.c. asphalt; Bronstein and Waller (U.S. Pat. 1188244, &c., 1916), several explosives consisting of mixtures of nitrostarch with ammonium nitrate, barium nitrate, trinitrotoluene, and sulphur; and Treese (U.S. Pat. 1265975, 1918), a blasting explosive containing 26 p.c. nitrostarch, 11 p.c. potassium nitrate, 22 p.c. potassium chlorate, 13 p.c. yellow wax, 7 p.c. soup stock, and 21 p.c. sulphur.

Nitrodextrin, prepared similarly to nitrostarch, has been proposed for use with ammonium nitrate in safety explosives, mixed with a little resin.

Nitromannite or Nitromannitol, a nitric ester $C_6H_8(NO_3)_6$, prepared by the action of the usual mixed acids on the hexahydric alcohol mannitol, extracted from manna, the dried sap of the manna ash (*Fraxinus Ornus*) (Linn.). The nitrated product, after being well washed, and dried at 40°, crystallises from ether or alcohol in needle-shaped crystals, which are insoluble in water. It is a very sensitive and highly explosive compound, exploding at about 300°, and has been suggested as a substitute for mercury fulminate. It is more sensitive to friction and shock than nitroglycerin, and nearly as powerful and local in its effects as fulminate. It is stable when thoroughly purified, but this purification is difficult to obtain on the large scale, and the product is usually very liable to spontaneous decomposition.

Nitrosugars. Nitrosaccharose, nitro-cane sugar, or 'fulminating sugar,' was first obtained by Schönbein, by nitrating cane sugar with a mixture of 1 part of strong nitric acid and 2 parts of strong sulphuric acid at 12°, washing, and drying. It is a white, amorphous powder, soluble in water, alcohol, and ether. On gently heating, it softens, and can be kneaded, but on strongly heating, it explodes violently. It is very sensitive and has been proposed for use in percussion caps. It is, however, deliquescent, and, as prepared up to the present, very unstable. Cocking and Kynoch Expl. Co. (Eng. Pat. 2836, 1911) suggest the nitration of a solution of 20 parts of cane sugar, or invert sugar, in 80 parts glycerol, with an anhydrous mixture of 54 parts of sulphuric acid, and 46 parts of nitric acid. The manufacture is carried out as with nitroglycerin, but more thorough washing is necessary for complete stabilisation. The product is given successively 2 washings with water, 6 with a 2 p.c. solution of sodium carbonate, and 2 final washings with a 0·2 p.c. solution of sodium carbonate, all at 40°. The nitrated mixture is suggested for replacing nitroglycerin in blasting gelatin, gelatin dynamite, and gelignite. *Nitrolactose* is similar to nitrosaccharose, but can be crystallised from its solution in alcohol or ether. It has similar violently explosive properties, and is equally sensitive and unstable. *Nitroglucose*, with vegetable fibre and potassium chlorate and nitrate, is a constituent of *Keil's explosive*, and solid and liquid nitro products, obtained from molasses, have also been proposed.

Other nitro explosives, prepared by the nitration of a great variety of organic substances, such as wood, flax, hemp, jute, gelatin, resin, coal, &c., have been prepared, and several have been already mentioned as constituents of various explosive mixtures.

Amino, and amino-nitro explosive compounds. Ammonium nitrate may be considered as the simplest of the amino-nitro compounds. Glycocoll nitrate, the nitrate of aminoacetic acid, has been used in a propellant, and good results obtained. Its explosion may be represented by:

$$CH_2(NH_2)\cdot COOH\cdot HNO_3 = 3H_2O + 2CO + N_2$$

and its explosion constants have been compared with those of picric acid by de la Roque (Rev. de Chem. indus. 11, 5). The Westfalish-Anhalt-Sprengstoff. A. G. (Ger. Pat. 203190, 1907) suggested the dinitrodialkylamides for use in explosives. The nitrates of the aromatic amines, like aniline nitrate, are used as constituents (for example, Ceipek (Fr. Pat. 341021, 1904) mixes the latter with ammonium nitrate), but they do not contain sufficient oxygen to form explosives by themselves. Hermann (Ger. Pat. 176072, 1905) proposes condensation products of formaldehyde and the aromatic amines.

Picramic acid and the picramates, and the corresponding reduction products of trinitrocresol, were proposed by Turpin in potassium nitrate mixtures (Fr. Pat. 185034, 1887). Claessen (Fr. Pat. 355695, 1905) proposed tetranitromethylaniline and the ethyl compound, as detonating explosives, and Will (U.S. Pat. 827768, 1906) uses the same compound mixed with mercury fulminate. Nitramines of the anthraquinone series of various degrees of nitration and explosibility have been suggested by Scholl (Ber 1904, 4427), and von Schroetter (Eng. Pat. 8156, 1907) proposed hexanitrodiphenylamine and its salts, alone or in mixtures. Nitro derivatives of the condensation products obtained by heating primary aromatic amines with oxalic acid, and the nitro derivatives of aromatic diamines, such as pentanitrodimethylmetaphenylenediamine, have been claimed by the Soc. Anon. d'Explosifs, &c. (Fr. Pat. 391106 and 391107, 1907).

The nitration of aniline directly gives only poor yields of nitro derivatives, owing to secondary reactions, and the nitranilines have not been much used in commercial explosives. Ortho- and para-nitraniline can be prepared by the nitration of acetanilide, and then removing the acetyl groups (Holleman, Hartog, and v. d. Linden, Ber. 1911, 704), and metanitraniline by the partial reduction of metadinitrobenzene. The mononitranilines can be readily further nitrated. 2.4.6-trinitraniline, or *picramide*, is a powerful explosive, readily obtained by the further nitration of orthonitraniline, or by the action of ammonia on trinitrochlorbenzene.

Tetranitraniline, the four nitro groups being in the 2.3.4.6- positions, was obtained by Flürscheim (8th Int. Cong. App. Chem. 1912) by the reduction of metadinitrobenzene with aqueous sodium bisulphide, the product being readily nitrated by mixed acids at a temperature not higher than 70°. Its direct production from aniline is described by van Duin and van Lennep (Rec. trav. chim. 1917, 37, &c.). They dissolved 26 grams of aniline in 700 c.c. of conc. sulphuric acid, then cooled to −5°, and added a mixture of 16 c.c. of nitric acid of sp.gr. 1·49 with 80 c.c. of conc. sulphuric acid. The mixture was kept in the cooling mixture for 2 hours, and then 117 grams of potassium nitrate were added, the temperature being kept below 50°. The mixture, after standing for a day, was then heated to 50° for 1½ hours, and again allowed to stand for a day. The crystals of tetranitraniline were then filtered off, and washed first with 50 p.c. sulphuric acid, and finally with water, and dried.

The product, melting at about 207°, is best crystallised from acetic acid. It gives yellow crystals, melting at about 216°, but it does not melt without some decomposition. It is stated to be stable, but on boiling with water, or if recrystallised from acetone containing water, it is converted into trinitroaminophenol, and it is doubtful, even when pure, whether it will stand prolonged storage. Flürscheim states that it has an explosive power, as measured by the lead block test, greater than that of any other solid compound, but inferior to that of nitroglycerin. It is detonated by a weight of 5 kilos falling 35 cms. It is readily detonated, when loose or compressed, either alone or when mixed with nitrates.

Tetryl, or Tetralite, is an explosive compound of this class used in large quantities in detonators, and as a 'priming' or intermediary detonating agent for the less sensitive high explosives. It is made by nitrating methyl- or more usually dimethyl-aniline, and its commercial name was given on the supposition that it was tetranitromethylaniline. It is actually trinitrophenylmethylnitramine

$$C_6H_2(NO_2)_3\cdot NCH_3NO_2$$

one of the nitro groups being in the side chain, the other three being symmetrically placed in the nucleus. A specially purified form of the explosive is known in the British Service as 'Composition exploding,' or 'C. E.'

Manufacture.—The explosive is liable to be of inferior stability, and it is very necessary that the materials used in its manufacture should be as free as possible from foreign matter. The following method of manufacture is given by Langenscheidt (Zeitsch. Ges. Schiess- u. Sprengstoffw. 1912, 445): the nitration is carried out in one stage in a jacketed enamelled-iron pot, fitted with an enamelled stirrer and a thermometer. 100 kg. of dimethylaniline, boiling very closely at 190°, is very slowly run into 1000 kg. of pure lead-free 97 to 98 p.c. sulphuric acid, the mixture being kept stirred and cooled. This solution, which should be of a clear light-brown colour, is without standing run slowly into 430 kg. of nitric acid of 47°B. strength, sp.gr. 1·483, kept stirred, and at a temperature of 40°. The reaction is violent, and the temperature is carefully kept below 44°, whilst two-thirds of the sulphuric acid solution are run in, after which it is allowed to gradually rise to 55°. The time taken for addition of the charge is 8 to 9 hours, after which the nitration is completed by further stirring for 2 hours at a temperature of 53°–55°. The nitric acid must not be stronger than stated, or large and less pure crystals are produced. The mixture is allowed to cool overnight, and the waste acids are run off. The crystals are washed on a vacuum filter, first with dilute sulphuric acid, and then with water until quite free from acidity, and rapidly dried. The crude product melts at about 126°–127°.

Purification.—It is necessary to further purify the product. This is done by recrystallisation from a suitable solvent, frequently benzene of a high degree of purity. The crude tetryl is dissolved in the boiling benzene, the solution filtered, and allowed to crystallise rapidly in a cooled pan, the mother liquor run off, the crystals washed with benzene, and dried in the washing vessel. The benzene is recovered by distillation under precautions, as the contained impurities are of an unstable and explosive character. It is also purified by crystallising from its solution in acetone, and an inferior grade from nitric acid. The last traces of acid can be removed by boiling with water, but prolonged boiling causes appreciable decomposition with the formation of picric acid.

Properties.—The purified tetryl is in the form of very fine pale-yellow crystalline powder. It is practically insoluble in water, but readily soluble in acetone, ether, and benzene, the best solvent being benzene. The melting-point of pure tetryl is 129·1°. It is distinctly more sensitive to blow than picric acid, being detonated on an anvil by a blow from a hammer, and is also more powerful. According to Langenscheidt, it can be exploded by a 5 kg. weight falling 30 cms. When strongly heated it burns fiercely with a very hot but smokeless flame, and 'puffs off' when projected on to a red-hot iron plate. It is readily detonated by a small charge of fulminate. It is not only a very powerful explosive, but has great shattering power, its velocity of detonation being of the order of 7000 metres per second. When compressed to a density of 1·6 its detonation velocity is 7200 metres per second, being slightly higher than that of picric acid at a density of 1·5. It is an excellent initiator of detonation in less sensitive explosives, being used for this purpose either as crystalline powder, granulated or 'corned,' or compressed into pellets. It is characterised by its high nitrogen content, 25·5 p.c., as compared with the 18·5 p.c. of trinitrotoluene, and is endothermic. It has been used to some extent in explosive mixtures, for example, in the ammonium nitrate explosive 'Fortex.' It is non-poisonous, but it has an extremely irritant action on the skin and mucous membranes, some persons being more susceptible than others. In some cases a most painful rash is produced, for which one of the best remedies is boro-calamine lotion.

Hexanitrodiphenylamine

$$(C_6H_2(NO_2)_3)_2NH$$

has been used to some extent as a high explosive for bombs by the Germans, usually with the addition of a little trinitrotoluene. It is a stable light-yellow powder, melting at 238°. It is insoluble in water, and not at all readily soluble in the usual organic solvents. It can be recrystallised from boiling glacial acetic acid. It has about the same power and sensitiveness as picric acid, and has the same drawback: that it is acid and readily forms sensitive salts with metals. It has an extremely irritant action on the skin.

Diazo explosive compounds. All the diazo derivatives are very sensitive explosive compounds. '*Chromate de benzine diazotée*' $C_6H_5N_2HCrO_4$ is one of a class of explosive compounds proposed as detonants by Caro and Griess (Eng. Pat. 1956, 1866). The diazo compounds generally are too sensitive and highly dangerous to be used in practical explosives.

Azo compounds. The azo compounds are more stable than the diazo compounds. They do not form explosives in themselves, but have been proposed in mixtures. For example, Girard (Fr. Pat. 349635, 1904) uses azobenzene mixed with dinitrotoluene or picric acid in chlorate and ammonium nitrate mixtures, in order to lower the melting-point of the nitro compound, and effect incorporation at a lower temperature.

Hydrazines. Hydrazine chlorate and perchlorate have been prepared by Salvadori (Gazz. chim. ital. 1907, ii. 32); they are highly explosive and sensitive compounds, the perchlorate being the more stable.

Hydrazoic acid, or azoimide HN_3, is one of the most explosive substances known. It is a volatile liquid, the vapour of which detonates on contact with a flame. The aqueous solution of the acid forms metallic salts; those of the heavy metals being extremely explosive. With ammonia it forms a white crystalline solid $HN_3{\cdot}NH_3$, which is less explosive. It burns away rapidly but not explosively, unless confined.

Azides. The heavy metal salts of hydrazoic acid, such as lead and silver azide, are sensitive explosives, and have considerable detonative power. The lead salt has greater power than mercury fulminate in initiating the explosion of many nitro explosives, and has been increasingly used in recent years in composite detonators, especially in Germany. Nickel azide is also particularly sensitive to friction, and is violently explosive. The azides have been prepared, and their explosive properties studied by Wöhler. The insoluble azides are prepared by double decomposition from sodium azide, which is manufactured either by the sodamide or hydrazine process, and the soluble azides by the action of hydrazoic acid on the carbonates or basic oxides of the metals in the presence of ether (Ber. 1917, 586). The soluble azides are readily hydrolysed in solution giving basic precipitates. The sensitiveness of the azides to heat and percussion has been determined by Wöhler and Martin (Zeitsch. angew. Chem. 1917, 33). They found that the azides of metals of low atomic weight are more hygroscopic, and have generally lower temperatures of ignition than those of high atomic weight, and that the azides of the alkaline metals exploded without true detonation. Some of the explosion temperatures found were: calcium azide, 158°; nickel azide, 200°; mercury azide, 281°; silver azide, 297°; lead azide, 327°. As usual, the results depended on the conditions of experiment, and the ignition temperatures quoted were the temperatures at which 0·02 gram of the salt detonated after an interval of 5 seconds. The azides of lithium, sodium, and potassium could not be exploded by percussion, the azides of barium, strontium, and calcium only exploded with flame, but the azides of the heavier metals gave true detonation with sufficient blow. In thin layers the sensitiveness of the azides to percussion was in the same direction as the sensitiveness to friction, the azides of the heavy metals being the more sensitive. Contrary to the results obtained with most explosives, the azides of lead and mercury were found to be more sensitive in thick than in thin layers, a result which accords with the property stated to be shown by their large crystals of spontaneous detonation.

Lead azide PbN_6 is manufactured on the large scale from the sodium salt by double decomposition with a soluble lead salt, such as lead nitrate or acetate. The solutions of the two salts are kept strongly agitated so that the lead azide is precipitated in the form of fine crystals. The precipitated crystals are well washed with water till free from impurities, and dried in a current of dry air at about 50°.

Lead azide is less sensitive to friction or blow than mercury fulminate, the large crystals being more sensitive than the small, and it has a considerably higher ignition point. It is not rendered less sensitive by wetting with water. It is quite stable, except in the presence of acid fumes. Stettbacher (Zeitsch. ges. Schiess- u. Sprengstoffw. 1914, 341) gives the heat of decomposition of lead azide as 364 calories per gram, and the temperature of explosion as 3483°. It is practically the only explosive in actual use that is not an instance of oxidation.

The explosive properties of the *nitrogen halogen compounds* are well known, but these compounds are unsuitable for practical explosives.

Acetylene compounds. Many of the compounds formed by the action of acetylene on metallic oxides and salts are violent explosives, and have been proposed as detonating explosives. The white solid obtained by passing acetylene into an acid solution of silver nitrate has been claimed by the Société Anon. Dynam. Nobel (Fr. Pat. 321285, 1902) as a substitute for mercury fulminate in chlorate detonating mixtures, and that obtained from an ammoniacal solution of mercury nitrate has been proposed by Venier (Fr. Pat. 364461, 1906) for a similar purpose. The explosive properties of these two varieties of silver acetylide have been examined by Eggert (Chem. Zeit. 1918, 199). He attributes the difference in their explosive properties to the presence of occluded impurities, silver nitrate and oxide in the acid and ammonia products respectively, and the gas they yield on detonation. He found the acid product gave more gaseous product and greater explosive effect, and also that the 'acid' silver acetylide has greater disruptive power than silver fulminate, but less than silver azide, and attributes the differences to differences in velocity of detonation.

Safety Explosives.

Prior to about 1880, black gunpowder and dynamite were almost the only explosives used in mines and quarries; the former for mining soft coal or obtaining large blocks of rock, the latter for the harder materials and where shattering effects were desired. At the present time, although gunpowder is used in this country to the extent of more than half the total weight of mining explosives, kieselguhr dynamite has been largely displaced by blasting gelatin, and a large variety of other explosives have come into use, more especially the so-called 'safety explosives' used in 'fiery' coal-mines. The use of gunpowder in these mines is everywhere prohibited.

The following table, taken from the 39th Annual Report of H.M. Inspector of Explosives, gives the amount of different explosives used in mines and quarries in Great Britain in 1913:—

Explosive	Quantity used, lbs.	P.c. of total
Permitted explosives	11,051,231	33·0
Gunpowder	17,060,874	50·1
Gelignite	3,960,173	12·0
Gelatine Dynamite	474,922	1·4
Blasting Gelatine	297,907	0·9
Roslin Giant Powder	247,871	0·7
Cheddite	187,226	0·6
Nobel Polarite	149,593	0·5
Blastine	122,590	0·4
Saxonite	85,606	0·3
Dynamite, Stonax, and Matagnite Gelatine	23,947	0·1

Of the 'permitted explosives,' those most used, in order of quantity, were: Bobbinite, Samsonite, Arkite, Ammonite, Bellite, Monobel Powder, Rippite, Roburite, Stow-ite, Ammonal, Westfalite, Swalite, Faversham Powder, Carbonite, Excellite, Rexite, Cornish Powder, Kentite, Abbeite, Permonite, Dynobel, St. Helens Powder, Fracturite, Negro Powder, Fortex, Stomonal, Dreadnought Powder, Cambrite, Britonite, Dominite, Minite, Superite, and as many other varieties used in smaller quantities.

Owing to an ever-increasing number of coal-mine explosions, due to the ignition of fire damp or dust by the firing of shots, the British Government appointed a Commission, which recommended that the explosive should be surrounded by a jacket of water, but no attempt was made to devise a safety explosive. Subsequent to the English Commission, several of the Governments on the Continent also appointed Commissions, but the factors which render an explosive safe to use in contact with inflammable mixtures were not definitely settled, and even now they are not known with certainty. It has been found impossible to devise an explosive that is absolutely safe under all conditions, and at the present time there is, in this country, no special definition of a 'safety explosive,' except that it must pass the Home Office tests and be placed on the 'permitted list.'

According to the French Commission, in 1888, the factors determining the ignition of inflammable mixtures are the temperature of explosion of the explosive and the duration of the flash. They found that a mixture of marsh gas and air ignited at 650°, but that at this temperature the ignition was delayed ten seconds, and a much higher temperature was permissible, if of short duration. A safety explosive had to fulfil the conditions that the products of explosion were free from inflammable substances, and that the calculated temperature of explosion should be below 1500°. Explosives having a high temperature of explosion, such as nitroglycerin 3200°, guncotton 2600°, and collodion cotton 2060°, should be mixed with a material having a low temperature of explosion, such as ammonium nitrate, 1130°, so that the mixture comes within the prescribed limit. Three classes of safety explosives were introduced, the 'Grisoutines' containing nitroglycerin and ammonium nitrate, 'Blasting Powder P' containing collodion cotton and ammonium nitrate, and the 'Grisounites' containing nitrohydrocarbons and ammonium nitrate.

This temperature limit cannot, however, be rigidly applied; for 'carbonite,' the first safety explosive, invented in 1885, and at the present time one of the safest, had a temperature of explosion well above this limit. According to Bichel, the inventor of carbonite, the calculated temperature of the explosion is of no value in determining safety, but the maximum temperature of the products of combustion, the length and duration of the flame, and the velocity of detonation, are the determining factors. The amount of the explosive used and the physical and chemical nature of the products of combustion, for example, the proportion of incandescent solid particles, are of great importance (Glückauf, 1904, 35)

The Prussian Commission came to the conclusion that the quicker the explosion, the greater the safety; consequently, that kieselguhr dynamite and guncotton were safe, and that fulminate detonators could not ignite pit gas. But this view is no longer held to be true in all cases, for 'bobbinite,' a slow black powder mixture, is one of the safest and most extensively used safety explosives, whilst blasting gelatin is not safe.

The Austrian Committee defined a safety explosive as one that gives a short, but not bright, flame, and one that passes the usual gallery tests. Von Lauer, in Austria, stated that bore-hole shots that have done their work never ignite pit gas, and that the risk arises from blown-out shots and fissured coal, but this contention has not held good in all cases. Guttmann considered that the risk of a blown out shot is frequently due to the rapidity of the explosion being sufficient to ignite the gas mixture, owing to the heat produced by the compression and friction set up in the atmosphere by the explosion gases.

Testing galleries.—The question as to whether explosives are suitable for use in fiery mines is now chiefly decided by submitting them to a practical test, which is intended to simulate, more or less, the conditions of use in these mines. The exact nature of the test varies in different countries, and the severity of the test has, from time to time, been increased as the factors determining safety have become better understood, and the manufacture of safety explosives consequently become more perfected. Explosives at one time 'permitted' are occasionally removed from the list, as the conditions of test are made more stringent.

The test consists in firing a number of shots under definite conditions into an explosive mixture contained in a long gallery, the explosive passing the test when no explosion occurs. Most countries have one or more official testing stations, and many manufacturers of explosives have their own testing galleries.

A testing gallery, based on a private one at Hebburn Colliery belonging to some north-country private manufacturers, was established at Woolwich in consequence of the Coal Mines Regulation Act, 1896, to test explosives proposed for use in coal-mines. This was amended by the Coal Mines Order of August, 1905, and by a later Memo. in May, 1912, in which the tests for 'permitted' explosives were revised, with the result that the testing station was removed from Woolwich to Rotherham. Those that pass this test are put on the list of '*permitted explosives*,' which indicates, not that they are absolutely safe under all conditions of use, but that they are safer than those not on the list. It is, indeed, recognised that all explosives, used under certain conditions and in sufficient quantity, will ignite mixtures of pit gas or coal dust and air.

In testing, a given weight of the explosive is fired from a gun into a mixture of 85 p.c. air and 15 p.c. coal gas. The shot is 'stemmed' with a definite length of dried pottery clay. These conditions at Woolwich are not intended to exactly imitate the actual conditions obtaining in a fiery mine, but rather to give a severe test which can be uniformly reproduced at any time. It is for this reason that coal dust is not employed in the Woolwich test.

The Woolwich testing gallery is an iron tube 2 feet 6 inches in diameter and 28 feet in length, with seven safety-valve orifices at equal intervals along the top of the tube, to allow the escape of the gas following an explosion. The shot is fired from a gun at a definite angle with the roof. Such a weight of the explosive is fired as is equivalent in strength to 4 ozs. of dynamite No. 1. The charge was determined previous to 1900 by finding the weights necessary to give equal enlargements in the lead-block test, but since that time the relative strengths of the various explosives has been measured by a ballistic pendulum test, which has been found to give more accurate results. One of the guns is charged with the explosive and fired from a fixed distance into the muzzle of a 5-ton mortar of 13-inch calibre suspended in an iron framework from an overhead beam. The swing of the mortar gives a measure of the strength of the explosive.

If the gas mixture does not fire in 20 shots, 10 shots with 12 inches' stemming and 10 shots with 9 inches' stemming, no explosive being left unconsumed, the explosive is considered safe. The size of detonator and nature of the wrapping to be used with the explosive are defined, as these are found to materially affect the results. For instance, explosives containing sulphur are much less safe in a lead alloy case than in a paper wrapper.

Any explosive, if fired in sufficient quantity and unstemmed into a mixture of coal gas and air, would cause the ignition of the mixture, and as early as 1903, Watteyne, of the Belgian testing station at Frameries, suggested that the highest charge which in a given number of shots failed to ignite the mixture used in the testing gallery, called the 'charge-limite,' should be taken as a measure of safety of the explosive, and some idea of the order of safety of different explosives obtained. This idea was generally adopted except in England, and this and other differences in the conditions of testing led to the English and Continental systems giving very different results, and many explosives passed by the one were condemned by the other. The present system of testing in England conforms more closely to Continental practice.

In 1912 the conditions of testing in England were altered, and a more modern station was erected at Rotherham, the old station at Woolwich being closed in February, 1911. The Rotherham gallery is an iron tube, 5 feet in diameter, and 50 feet long. The bore of the cannon is 4 feet long and 2 inches in diameter. The capacity of the gallery is 354 cubic feet, and the proportion of coal gas used in the mixture is 13·5 p.c. Coal-dust is also used, 40 ozs. being spread on a board in the first 10 feet in front of the cannon, and a further 80 ozs. placed in heaps along the remaining 40 feet of the gallery. The coal used is of a particular quality, giving 2·4 p.c. moisture, 29·6 volatile matter, 65·4 p.c. fixed carbon, and 3·94 p.c. ash, and is ground to pass a 150 mesh sieve. No tamping is used in this test, the charge being fired directly into the explosive mixture of coal gas, coal-dust, and air. The largest charge which fails to fire the mixture in one of five shots is known as the 'maximum' charge, and this must not be less than 8 ozs. The explosives are made up into cartridges of 1⅜ inch diameter, so that they occupy only half the sectional area of the bore.

The ballistic pendulum at Rotherham weighs 5 tons 1 cwt., and has a bore of 13 inches; the radius of swing is 7 feet 8 inches, and the bearings are made as frictionless as possible. A charge of 4 ozs. of the explosive is loaded into a cannon, stemmed with clay, and fired close up into the mouth of the pendulum, the back swing of which is recorded in inches.

On the Continent, similar testing stations exist, the first testing station being built by the Prussian Government at Neunkirchen. The galleries are long wooden or iron tubes, round or oval in section, but usually considerably larger in section than the Woolwich gallery. At first the explosives were suspended in the gas mixture for firing, but the mixture under these conditions always fired, and the method of firing into the mixture from a small cannon, was adopted. The galleries vary in sensitiveness according to their diameter, material, and situation; and the results obtained at one gallery are not directly comparable with those obtained at others. A particular gallery will also give irregular results on certain days, for reasons that have not been explained, but atmospheric pressure is probably a considerable factor, and results obtained on these days have to be neglected. The explosive mixture generally used is prepared with natural pit gas, but occasionally artificially prepared methane, coal gas, or even benzene vapour is used, and usually coal-dust is suspended in the explosion mixture. Coal-dust is said not to increase the sensitiveness of the mixtures, but causes the ignition to be more violent and therefore more visible. Beyling showed experimentally (Glückauf, 1908, 1717) that all explosives ignite either coal-dust or a gas mixture more readily than a combination of the two, and in Germany safety explosives are not now tested, as formerly, in a gas mixture containing coal-dust, but in fire-damp (8 to 9 p.c.) and coal-dust mixtures separately. The cannons used vary in bore, and it has been found that the narrower the bore of the cannon, the easier the ignition. At the United States testing station at Pittsburgh, the gallery is a steel cylinder, 100 feet long, and 6⅓ feet diameter. The gallery is filled with either coal gas and air, coal-dust and air, or coal gas, coal-dust and air. The Belgian gallery at Frameries is a wooden cylinder, 30 metres long, and 2 square metres in sectional area. The bore of the cannon is 46 cm. long and 5·5 cm. diameter. A mixture of coal gas, coal-dust, and air is used.

The general method in use is to find the *charge-limite*, or maximum charge of the explosive which, in a series of 10 shots, just fails to fire the explosive mixture, the charge being unstemmed. The conditions for use of 'permitted' explosives are frequently defined. They must be used with a certain No. detonator, an explosive ceases to be 'permitted' if it is frozen, and the nature of the wrapping and stemming, combustible or otherwise, may be laid down.

Composition.—By far the greater number of safety explosives are either nitroglycerin mixtures or ammonium nitrate mixtures. Sometimes the mixtures contain both ammonium nitrate and nitroglycerin, so as to combine the advantages of the two types. Some black powder and chlorate and perchlorate mixtures are also used. The proportion of oxygen is frequently kept low so as to reduce the temperature of combustion by burning the carbon to monoxide only, but the objection to this is the poisonous and combustible nature of this product.

The nitroglycerin explosives, containing a little nitrocotton to gelatinise them, have a high charging density, are readily detonated, and are waterproof. The latter quality enables them to be used in damp or wet bore holes. They are plastic and can be well rammed into the bore holes, thus assuring a maximum effect. They are specially useful in blasting the harder materials. The safety of these explosives varies inversely with the proportion of nitroglycerin, and the maximum permissible is about 30 p.c. The nitroglycerin explosives are not so safe against percussion, such as an accidental blow, or too hard ramming, as the ammonium nitrate explosives; and when so ignited not only does the whole cartridge explode, but the explosion may be communicated to the adjacent cartridges. Another drawback is their liability to freeze.

The ammonium nitrate explosives, which give a large volume of gas at a comparatively low temperature, are very safe, because of the large amount of water contained in the products of explosion, but they are difficult to detonate completely, and usually their hygroscopic nature necessitates the use of a waterproof wrapper. They are so difficult to ignite and so insensitive to percussion, that their transport is quite safe, but their charging density is low and their effect less than that of the nitroglycerin explosives. When ammonium nitrate explosives do fire by percussion, only that portion actually struck is ignited. They necessitate the use of large bore holes, and are consequently best adapted for blasting soft materials. Ammonium nitrate itself is quite safe in any quantity, and the safety of mixtures prepared with it depends on the nature and proportion of the combustible material.

Ammonium nitrate explosives containing a small percentage of nitrocellulose, have been thought, especially in Austria, to be amongst the safest, but they are not permitted in this country. The reason for this is that they are liable to slowly decompose and become acid, and the liberated acid and ammonia attack and decompose the nitrocellulose.

Both Dautriche and Taffanel have established that, by the addition of potassium nitrate to safety explosives, the factor of safety in pit gas mixtures is considerably increased, whether the temperature of explosion be high or low. The heat of combustion is considerably lowered, whilst the explosive force is not appreciably diminished (Taffanel, Zeitsch. Ges. Schiess- u. Sprengstoffw. 1910, 305, &c.).

Safety ingredients.—In safety explosives, the ingredients are so proportioned that the carbon is mainly converted into carbon monoxide. This reduces the temperature of the explosion without sensibly diminishing the explosive force, owing to the increased volume of gases produced. The principle of safety explosives is, further, so to arrange the nature and proportion of the ingredients that a sufficient volume of non-inflammable gas, such as water vapour, carbon dioxide, nitrogen, ammonia, &c., is produced to dilute the carbon monoxide and prevent its contact with the air until its temperature has fallen below the ignition-point.

As already mentioned, the first suggested remedy for the prevention of the ignition of fire-damp was to surround the cartridge with a water-jacket. Subsequently it was found that tamping the explosive with wet moss, sawdust saturated with a solution of alum or ammonium chloride, sand, or clay added considerably to the safety; tamping even with only 1 inch of dry sand was shown by Guttmann to double the safety.

The use of wet tamping materials led to the use of salts containing large quantities of water of crystallisation, such as sodium carbonate and magnesium sulphate, or salts which liberate much water at the temperature of explosion, such as ammonium oxalate.

A large percentage of sodium carbonate is used in 'wetter dynamite' and 'Grisoutine,' and ammonium oxalate in 'securite.' Magnesium sulphate has not been much used because of its effect on the miners.

Another class of additions is salts which dissociate and absorb heat at the temperature of explosion. Examples of this class are the potassium dichromate in 'dahmenite' potassium permanganate in 'roburite,' and ammonium chloride in 'antigrison.' The use of ammonium chloride led to the production of hydrochloric acid in the mine gases, and it was consequently mixed with an equivalent quantity of sodium or potassium nitrate; or better, the alkali chlorides are themselves used (Bichel, Fr. Pat. 327868, 1902).

Modern German safety explosives contain large proportions of potassium or sodium chloride, and these explosives are very safe, especially in coal-dust mixtures, but are not so powerful as the older explosives.

The use of materials which absorb heat on decomposition, such as wood pulp and rye flour, has been found to confer great safety on explosive mixtures containing them, such as 'carbonite' and 'gelignite.'

The good effect of wood meal led to the manufacture of those safety black powders, like Argus powder and earthquake powder, containing a high percentage of volatile matter (*see* Curtis and others, Eng. Pat. 17878, 1898, and 6523, 1899). Some of the good effect of these slack-burnt charcoals has also been attributed to their reduced content of solid matter. Curtis and others (Eng. Pat. 6756, 1898) claimed the use of a layer of sodium bicarbonate in front of an ordinary gunpowder charge, the safety action depending on the liberation of carbon dioxide. The Westfälisch-Anhalt. Sprengstoff. Actien-Gesells. (Eng. Pat. 3334, 1902) compound an explosive mixture so as to produce a large volume of ammonia on detonation; Reschke (Eng. Pat. 25780, 1905) suggests copper oxalate; von Dahman (Eng. Pat. 7562, 1898) suggests the use of acetic, citric, or tartaric acid and their salts with such explosives as roburite; Callenberg (Fr. Pat. 322946, 1902) proposes to add turpentine chloride; Macnab proposed to insert a glass tube containing aqueous ammonia into the gunpowder cartridge.

TESTING EXPLOSIVES.

The explosive characteristics of a powder depend primarily on its chemical nature. The analysis of explosives is consequently of great importance. As far as space would permit, an outline of the analysis has already been given under the individual explosives.

The purity of the ingredients, size of the grain, intimacy of the admixture and density, also largely influence the character of the explosive. A microscopic examination of a mechanical mixture, as with the cap composition, is of value.

An eye inspection of explosives that have been in store should be made for any sign of efflorescence and deliquescence or exudation, if a nitroglycerin explosive; and for signs of cracking or breaking down, in nitrocellulose powders; or local patches of discoloration in nitro powders generally. The development of acidity, as shown by the reddening of blue litmus paper, often indicates decomposition.

Stability Tests for Nitro Explosives.

One of the most desirable properties in explosives, whether for use as propellants or disruptives, is that they shall be chemically stable under all the conditions of climate, storage, and transport that they may have to withstand. All nitro explosives undergo decomposition at temperatures below, in some cases considerably below, their exploding-points, even when pure, and many of them are liable to contain traces of acids and impurities that are much less stable. The decomposition of these impurities leads to the production of higher oxides of nitrogen which act catalytically on the explosive itself, and may lead to the spontaneous ignition of the latter.

The extensive use of guncotton, dynamites, smokeless powders, and other nitro explosives necessitates the use of tests that will not only determine the stability of the ingredients themselves, but also detect the presence of any unstable impurities. The test should also be simple and reliable, and only take a short time to carry out. No single test has been devised that is universally applicable and will satisfy all these requirements, and it is usual to employ two, three, or more of the numerous tests that have been worked out and to form a definite conclusion on the combined results.

Vieille concluded from his results with the French 'Poudre B.' that the life of a propellant could be calculated from the rule that a life of 1 hour at 100° = 1 day at 75° = 1 month at 40° = 1 year at 17·5°. This rule is expressed by the formula $L_t = L_T 1{\cdot}10^{T-t}$, where L_t is the life at the storage temperature $t°$, and L_T the life at the temperature T° of the stability test. The rule is approximately true with the reservation that the coefficient 1·10 varies slightly with the nature of the propellant, its composition, and method of manufacture.

Unless otherwise mentioned, the tests apply only to nitrocellulose or nitrocellulose powders.

Deflagration test. One of the earliest tests was that devised by Hess. The explosive was heated at a fixed high temperature, and the time of evolution of coloured fumes and also of firing was noted. In a modified test, the explosive was heated under pressure at 75° till explosion took place. This test, which is, at best, only a very rough indication of stability, is not much used at the present time, but is the basis of several other tests.

Fume test.—The test, devised by Thomas, consists in heating a definite weight of the explosive at a definite elevated temperature until brown fumes appear, the stability of the explosive being judged by the time taken. The method of carrying out the test with guncotton is as follows: 2·5 grams are weighed out into a well-cleaned glass tube, 32 cm. × 1·6 cm., and pressed down to a height of 4 cm. The tube is closed by a well-fitting glass stopper and placed to a depth of 10 cm. in an oil-bath, heated to 135°. At the end of 10 minutes, any moisture condensed on the upper part of the tube is wiped out. A standard tint for fixing the end of test is made by filling a tube with a solution containing 8 mgms. of potassium dichromate and 0·4 gram of cobalt sulphate per litre. The test is an official one in France and Holland, and is frequently used in combination with other tests; the temperature of the test being varied.

An objection to it is the length of time it takes for completion; for example, as used in Holland, guncotton heated for 10 hours a day at 95° requires 21 days before red fumes are developed.

Abel heat test is the English official heat test applied to nitro explosives generally, and is defined by the Explosives Act, 1875. The principle of the test is to note the time required to produce a standard discoloration of a test potassium iodide-starch paper, when the explosive is heated under specified conditions. The explosive is weighed out into test-tubes, about 5½ to 5¾ inches long, and holding 20 to 22 c.c. when filled to a height of 5 inches, which are closed by an indiarubber stopper, fitted with a glass rod terminating in a platinum wire hook. On the hook is suspended a test paper, about 10 × 20 mm., the upper half of which is moistened with a mixture of equal parts of glycerol and water. The test papers, on the correct preparation and sensitiveness of which the test depends, are now made by the Home Office and by the War Office, and supplied to manufacturers of explosives. The test-tubes are placed to a depth of 3 inches below the cover, in a water-bath, the temperature of which is carefully regulated, at usually 160° or 180°F. The water-bath is a spherical copper vessel, about 8 inches in diameter, fitted with a cover having a number, usually six, of circular holes, fitted on the under side with clips to take the tubes. The bath is fitted with a thermometer, the bulb dipping 2¾ inches into the bath, and usually some form of temperature regulator. The test is complete when the faint brown line which appears at the junction of the wet and dry parts of the test paper, which is adjusted to be ⅝ inch above the cover, is equal in tint to the brown line on a standard-tint paper. This standard tint is a line drawn on paper of similar make to unprepared test papers, with a solution of caramel in water of defined strength.

The English Government specifications require that nitroglycerin displaced by water from dynamite, shall stand for 15 minutes at 160°F. (71°C.); blasting gelatin and gelatin dynamite 10 minutes at 160°F.; cordite and ballistite, 15 minutes at 180°F. (82°C.); guncotton and tonite, 10 minutes at 170°F. (76·6°C.); and gelatinised guncotton preparations for 15 minutes at 180°F. Smokeless powders are ground in a mill and sifted, and the portion retained between two sieves having holes equal to 14 and 21 B.W.G. respectively is used for the test.

In the United States, the first appearance of a brown line is taken as the end of the test, and the specified times are nitroglycerin, 15 minutes at 160°F.; blasting gelatin dynamite, 10 minutes at 160°F.; nitrocellulose for the Army 40 minutes, for the Navy 30 minutes, at 150°F. (65·5°C.); guncotton from compressed blocks, 10 minutes at 150°F.; nitrocellulose powders, 10 minutes at 100°F., and nitroglycerin-nitrocellulose powders, 20 minutes at 150°F.

In Germany, zinc iodide is used instead of potassium iodide in the preparation of the test papers, which are more sensitive than those prepared with potassium iodide.

This test is, perhaps the most generally applicable and most frequently used. Objections that have been raised to it are that it is purely empirical, and depends largely on the conditions of its application, and further that it is really a test for traces of unstable impurities, and not of the absolute stability of the explosive itself.

Guttmann, in 1897, pointed out that the Abel test could be masked and falsified. With an explosive containing residual solvent, such as acetone, the test depends on decomposition of the nitro compounds, combined with the retarding influence of the solvent. In a similar way, the small quantities of stabilisers added to nitro explosives influence the time of test.

This is of little importance so long as these masking agents are recognised constituents of the explosive and present in their normal amount, or are extracted before the test is taken, as the limits of the test are fixed accordingly.

Mercuric chloride, which has a very strong masking influence on the heat test (as little as one part in 50,000 appreciably lengthens the heat test of cordite) is, in some countries, a recognised constituent of certain guncotton explosives, with the idea of sterilising them, but its use is not permitted in this country.

Modifications of the Abel test have been suggested, principally with a view of obviating the influence of masking agents. Guttmann (J. Soc. Chem. Ind. 1897, 287), for example, proposed a test paper treated with diphenylamine dissolved in sulphuric acid, which gives an intense blue colour with traces of nitrous acid; and Hoitsema (Zeitsch. angew. Chem. 1899, 705) proposed the same reagent used in a different manner. This indicator works well with guncotton explosives, but with nitroglycerin explosives the results are erratic, and they can also be readily masked.

Metaphenylenediamine was suggested as the best reagent by Spica, in 1899, but this again does not seem to work well with nitrocellulose-nitroglycerin explosives, and neither of the proposed modifications has been adopted.

Silvered-vessel test. This test was devised at the Royal Gunpowder Factory, Waltham Abbey, to give an idea of the amount of deterioration that a sample of cordite had suffered, and from this to judge the further length of time it would be safe to store the cordite at any given temperature.

A silvered vacuum-jacketed flask is filled with the ground sample of cordite and exposed in a bath heated to a constant temperature of 80°. Readings of a thermometer, the bulb of which is in the centre of the cordite, are taken at intervals until the temperature rises 2° above that of the bath. The time taken for this rise of temperature of 2° is a measure of the stability of the cordite. The flask is fitted with a side tube in the neck, and the appearance of brown fumes in this tube indicates the active decomposition of the cordite, and serves as a warning that the test is near completion.

From the time of the test in hours, using a factor that has been established connecting rate of increase of deterioration of cordite with rise in temperature, the length of serviceable life of the cordite at any particular temperature can be calculated.

A newly made Mark I. cordite has a S.-V. test of from 500 to 600 hours.

German test.—In this test, which is largely used on the Continent and is one of the American Service tests, 2·5 grams of the air-dry explosive are heated in a glass tube loosely closed with a perforated cork at a fixed temperature, until a folded piece of litmus paper, fixed at 0·5 inch above the explosive, is completely reddened. The temperature of the test is 135°. The time limits are fixed by tests with standard samples of the particular explosive. Besides the time of complete reddening of the litmus, the time of the appearance of brown fumes and the time before the sample explodes, are also noted.

The American limits for this test are: for nitrocellulose and nitroglycerin powders, complete reddening over 30 minutes, brown fumes over 45 minutes, explosion over 5 hours; and for colloided nitrocellulose, complete reddening over 75 minutes, brown fumes over 2 hours, and explosion over 5 hours.

Vieille test.—This test is the French Service test. 10 grams of the explosive are weighed out, and a piece of standard blue litmus paper is also introduced into a glass tube which is closed as tightly as possible by means of a clamped well-fitting stopper. The tube is heated in a bath maintained at 110°. When the litmus paper is completely reddened, the time is noted and the tube cooled. The sample with a fresh piece of litmus paper is introduced into a second tube and the heating continued. This process is repeated until a period of less than an hour is taken to completely redden the litmus paper. The sum of the number of hours of the previous heatings is then taken as the time of the test.

Vieille found that, as the temperature of the test was raised, the time is reduced in arithmetical progression, and concluded that 110° is the best temperature for giving reliable results within a reasonable time.

'Poudre B' has a Vieille test of approximately 50 hours.

There is a gradual loss of nitrogen from the powder during the test which Vieille found to be approximately 0·009 p.c. nitrogen per hour, during a test of 100 hours (Mém. des Poudres et Salpêtres, 1909, 71). The decrease in the nitrogen content, and the time taken to first redden the test paper, are both considered in conjunction with the total time of the test in sentencing a powder.

Will test.—This test gives a quantitative idea of the stability of a nitrocellulose, and is very largely used in conjunction with such tests as the Abel test. The test, which is fully described by Will in the Mitt. aus der Centralstelle f. Wissensch. Tech. Untersuchungen, 1900, [2] 5, and 1902, [3] 34, is based on the measurement of the nitrogen evolved from guncotton when heated at a temperature of 135°. 2½ grams of the dry nitrocellulose, or 3½ grams of moist nitrocellulose as it leaves the centrifugal machines, are weighed out into a glass decomposition tube and compressed to a given volume. This tube is connected at one end with a preheating glass coil, and is fitted at the other end with a well ground-in exit tube. The tube is placed in an oil-bath fitted with a stirrer, the temperature of which is carefully regulated to 135°. To remove the products of decomposition as fast as they are formed, a uniform current of purified, air-free, carbon dioxide is passed over the heated nitrocellulose at a rate of about 25 c.c. per minute. The gases after passing over heated copper gauze, contained in a heated copper U-tube, to reduce the oxides of nitrogen, are collected over caustic potash in a gas burette, with a special zigzag arrangement to give thorough absorption of the carbon dioxide. The column of the nitrogen collected is read off first after 30 minutes, then after every 15 minutes for a period of about 4 hours, the caustic soda being frequently renewed. Explosions may occur, and the oil-bath is surrounded by a strong screen. The results are plotted on a curve. The gas from a stable nitrocellulose should be evolved at a uniform rate, and, if this is so, Will considers that the sample is normal, or has attained a 'limit-state' of purification.

With unstable samples, the gas evolution is much greater at first than later in the test.

To interpret the results given by any nitrocellulose explosive, a set of standard curves must be obtained from well-purified samples for purposes of comparison. English Service gun cottons average an evolution of 7·5 mgms. ± 1 mgm. of nitrogen per 4 hours (Robertson).

Reiss test. This is a modification of the Will test, in which the decomposition is effected at 135° *in vacuô.*

This modification is the one usually applied to high explosives of the nitro class, the temperature of the bath and time of heating varying with the explosive. The decomposition tube is connected by means of a well-fitting stopper, having a mercury lute with a long mercury manometer tube in which the gas volumes are read off at intervals for some days, and the results, corrected to N.P.T., plotted and interpreted by reference to curves obtained from standard samples

Obermüller test. This test is similar to the last, except that the gas volumes are not calculated, but the pressures exerted by the evolved gas, the volume of which is kept constant, are recorded. The rate at which the pressure increases is taken as a measure of the decomposition, and so of the instability of the explosive. For nitrocellulose, the temperature of the test is 140°. Mittasch (Zeitsch angew. Chem. 1903, 929) describes a similar test in which the gas evolution is automatically recorded.

Bergmann and Junk test.—This test gives very reliable results, and has been largely used, especially in Germany. 2 grams of the dry nitrocellulose are weighed out into a tube 35 cm. long and 2 cm. wide, and pressed down. The decomposition tube is connected with a ground-glass stopper connected with an absorption bulb containing water. The explosive is heated for 2 hours in a bath, kept at a constant temperature of 132° by boiling amyl alcohol. The decomposition tube is then allowed to cool, and the water to flow back on the explosive. The contents of the tube and apparatus are washed and filtered, the filtrate oxidised with permanganate, and the nitrogen estimated as nitric oxide by the Schulze-Tiemann method. The limits of gas evolution fixed are 2·5 c.c. of NO per gram guncotton, or 2 c.c. per gram collodion cotton. This test is considerably influenced by the amount of moisture present in the sample.

Sy test.—This is a U.S. Service test (J. Amer. Chem. Soc. 1905, 549). 1 to 4 grams of the explosive are weighed out on a covered watch glass and heated in an air-bath, maintained at a constant temperature of 115° by a boiling mixture of xylene and toluene. After 8 hours' heating, the watch glass is cooled and weighed, and the process repeated daily for some six days or more. The daily loss in weight, mgms. per 1-gram sample, is plotted out, and comparison made with standard curves. The advantages claimed for this test are that whole pieces of the powder are tested, and that all volatile products of decomposition are determined.

Jacqué test is a modification of the above, made in order to reduce the time of the test (Zeitsch. Ges. Schiess- u. Sprengstoffwesen, 1906, 395). The sample is heated at 130°–140°, and weighed after successive 2 hours' heating.

Intensity of Action of Explosives.

The intensity of action of an explosive depends on the volume of gases produced, on their temperature, and on the velocity of explosion or detonation of the substance.

Closed-vessel experiments.—The 'strength' of an explosive may be calculated by Berthelot's 'characteristic product,' QV_0, where Q is the heat of explosion of unit weight, and V_0 the calculated volume of the gaseous products of explosion at 0° and 760 mm. pressure. The results so obtained are generally in the same direction as the results experimentally obtained for 'strength' by the lead block test. The volume of permanent gases and the quantity of heat evolved have been determined for many of the more important explosives; but the gases collected and examined are those remaining after cooling down to atmospheric temperatures, not those existing at the period of maximum temperature. The uncertainty as to the nature and the specific heat of the products of explosion at the high temperatures produced, renders the calculation of quantity of heat into temperature hazardous. The experiments are carried out with different densities of charge in some form of steel bomb, similar to Berthelot's calorimetric bomb, as used in the experiments of Abel, Noble, Deering, Macnab, and others already mentioned, details of which are given in the papers referred to.

The pressures developed in the bomb are usually measured by a *crusher gauge.* This consists of a small steel cylinder, closed at one end, into which a collar screws gas-tight. A piston working through the collar fits against a small cylinder of copper resting on the bottom of the cylinder chamber. On firing the explosive, the gas pressure acting on the end of the piston compresses and shortens the copper cylinder. The pressure in tons per square inch corresponding to the reduction in length of the cylinder, accurately measured on a micrometer scale, is obtained from tables compiled from the compressions produced by various statical pressures. Other methods of measuring the pressure are used. Deering checked the results obtained with the crusher gauge by closing an orifice of the bomb with a steel ball held in position by heavy lead cylinders. The weight was gradually reduced until the pressure was sufficient to lift the load. Several pressure gauges have been invented for directly measuring the pressure. For example, Bichel (Eng. Pat. 18273, 1898) has designed a gauge, fitted into the explosion vessel, which records the pressure developed by means of a pencil working on a drum, rotating by clockwork. Some knowledge of the rapidity of the explosive is also obtained by the steepness of the curve recorded, and the pressure of the cooled gases is indicated when the curve becomes horizontal. From the latter and the volume of the chamber, the volume of permanent gases can be calculated. Petavel (Proc. Roy. Soc. 1905, 492) describes a method of measuring the pressure developed by explosives by means of a specially constructed manometer which records photographically on a revolving cylinder.

The attempts of Macnab and Ristori to experimentally measure the temperature of explosion have been already referred to. Bichel has attempted to obtain an idea of the temperature of explosion by taking spectrum photographs of the flames produced on detonation.

Information of value, concerning the intensity of action of explosives, may be obtained by detonating a charge (a pound or so in weight) buried in earth, and observing the size of the crater; or by noting the reaction effects (the dimensions of the crater) produced on undisturbed earth, or the bulge or hole produced in wrought-iron plates, by the detonation on them of the explosive; comparison being made with an equal weight of guncotton or other known explosive, the charges having the same area and shape (most conveniently cylindrical).

Lead cylinder method: Trauzl test.—In this method the enlargement of the cavity in a lead block of given dimensions gives a measure of the power of the explosive. Abel's results, quoted in this article, were obtained by this method, using cylinders of soft, pure lead, 12 inches high and 12 inches in diameter, with a central cylindrical hole 7 inches deep and 1·3 inches in diameter, in which 1 oz. of explosive is detonated. With cylinders of these dimensions, no cracking through of the bottom is to be anticipated; the diameter of the bore hole just takes a service 1 oz. dry guncotton primer, which is used as a standard of reference. The lead cylinder is placed on a stout iron plate, the weighed explosive (cast or compressed into a cake, or rammed to a known volume in the bore hole, according to circumstances) with a mercury fulminate detonator (or suitable priming such as will produce a maximum effect on detonation) inserted into it is placed at the bottom of the bore hole, the latter filled with fine sand poured into it without pressure, and the detonator fired electrically or by safety fuse. The volume of the cavity produced is ascertained by means of water and a graduated vessel, and the volume of the bore hole being deducted gives the enlargement. With an unknown explosive, several experiments are necessary to ascertain the best conditions of detonation. This test is only reliable for the comparison of explosives of the same type, and the results obtained with slow-acting explosives are of little value. The higher the velocity of detonation, the greater the expansive effect.

Standard conditions for carrying out this test were suggested by the 5th Inter. Congress of Applied Chemistry, Berlin, 1903. The standard dimensions of the lead cylinder are, height 200 mm., diameter 200 mm., with an axial bore hole 125 mm. deep and 25 mm. diameter. The lead must be pure and soft and the cylinders used in a series of tests must be cast from the same melt. The temperature of the cylinder must be uniform throughout and between 15° and 20°. 10 grams of the explosive are formed into a cartridge 25 mm. in diameter by wrapping in tinfoil, weighing 80–100 grams per square metre. An electric detonator with a charge of 2 grams is placed in the midst of the explosive. The charge is gently pressed to the bottom of the bore hole by means of a wooden stick and the bore hole filled up with dry quartz sand. After firing, the cavity is brushed out and finally measured.

Sand bomb method.—This method of testing the explosive power was developed for detonating explosives by Storm and Cope (U.S. Bureau of Mines, Tech. Paper 125). A detonator charged with the explosive under examination is fired, by means of a length of safety fuse or electrically, in the centre of 100 grams of sand contained in a cylindrical steel bomb, 21 cm. × 9 cm., cavity 15 cm. × 3·1 cm., fitted with a loose cover perforated for the firing fuse or wires. The sand used is a pure quartz sand, passing a 20-mesh sieve, and retained on a 30-mesh sieve. After the detonator has been fired the sand is sieved through a nest of five sieves of 30-, 40-, 60-, 80-, and 100-mesh to the linear inch, and the strength of the detonating charge determined by the comminution. It was found that the total weight of sand that passes the 30-mesh sieve after the test is a measure of the strength of the explosive. Storm and Cope found that the quantities of pulverised sand are directly proportional to the weight of explosive charge in the detonator, and also showed, for instance, that the strength of mercury fulminate and fulminate-chlorate mixtures of different proportions as indicated by this test, was in the same direction as their relative efficiencies in initiating detonation in other explosives.

Abbot's ring apparatus.—Many of the earlier values for the intensity of action of explosives were obtained by Abbot in the ring apparatus described in his classical report upon 'experiments and investigations to develop a system of submarine mines' (Washington, 1881). The explosive was contained in a suitable case fixed in the centre of a wrought-iron ring 4 feet in diameter into which six lead crusher gauges were fixed at equal intervals. The apparatus was submerged in deep water, and the explosive fired electrically. The explosive force was obtained as usual from the shortening of the lead cylinders.

McRoberts has described a method of comparing explosives by the reaction effect their detonation produces on a pendulum-hung mortar weighing about 600 lbs. The distance from the centre of suspension to centre of trunnions is exactly 10 feet; the mortar is set with its axis horizontal. 10 grams of explosive are placed in a small recess behind the chamber for the projectile; the latter weighs about 40 lbs. and fits the bore gas-tight. The explosive is fired by means of a fuse and detonator; the angle of recoil of the mortar is marked on a graduated index by a pencil which the former carries. The work done by the explosive is twice that done in raising the mortar through the versed sine of the angle of recoil; this is expressed in foot-pounds.

Detonative power and sensitiveness to detonation. The sand bomb apparatus used for detonating the explosive power is adapted for determining the detonative power or sensitiveness to detonation of explosives, as worked out by Taylor and Cope (U.S. Bureau of Mines, Tech. Paper 145). In this method a composite detonator, containing a fixed base charge of some nitro explosive, say trinitrotoluene or 'tetryl,' is primed with diminishing quantities of the detonating explosive, whose detonating power is to be tested, and fired in the bomb, the minimum quantity of the priming explosive necessary to give certain and complete detonation determined. The relative sensitiveness of various explosives to the initiation of the same detonant may also be determined in the same way, by using them as base charges in a parallel series of trials. 0·4 gram of the explosive is weighed out into a copper detonator shell, say 5 mm. diameter, and lightly compressed by means of a glass rod. The priming charge is then introduced, covered with a thin perforated copper reinforcing cap, 9 mm. long with 2·3 mm. perforations, and pressed down with a loading pressure of 200 atmospheres per square inch. Incomplete detonation is indicated by a small comminuting effect on the sand, and the presence of part of the unaltered base charge in the sand. For example, by this method it was found that trinitrotoluene is less sensitive to detonation than tetryl, the minimum charge of a priming composition of 9 : 1 fulminate-chlorate required for certain and complete detonation was for trinitrotoluene 0·25 gram, and for 'tetryl' 0·19 gram. The sensitiveness of trinitrotoluene was found to be increased by admixture with 'tetryl' in proportion to the amount added. Lead azide was found to be a particularly good detonant for tetryl.

The 'Esop test' is another method of determining the detonating power of explosives, the principle of which is to determine that mixture of picric acid with olive oil containing the highest proportion of oil that the detonator will just detonate.

Velocity of detonation. The old method of determining the rate of detonation was to place a number of cartridges end to end, pressed well in contact with one another, so as to form a continuous length of the explosive. This cord of explosive was fired at one end by some efficient detonating agent, and the time of explosion was taken by a Boulengé electro-ballistic chronograph, as described under 'Ballistics of a propellant,' the two electric currents being successively interrupted by the firing of the two ends of the cord.

The results of numerous experimenters showed that the velocity of detonation increased, up to a certain point, with the diameter of the train of explosive. These experiments required a large bulk of explosive, the train of explosive being usually about 3 cms. in diameter and 35 metres in length, so that they were both costly and dangerous to carry out.

Mettegang's recorder.—An improved, purely electrical method of determining the velocity of detonation was described by Mettegang, at the 5th Inter. Congress of Applied Chemistry, Berlin, 1903. It is a modification of Siemens' apparatus for measuring small intervals of time. The method depends on the consecutive interruption of two wires, carrying a divided current, running through two ends of a long cartridge and connected with a sparking induction coil. The main current passes through a resistance of electric lamps, and to ensure a high potential, no iron core is used in the primary. Any change in the tension of the current passing through the primary coil sets up an induced current in the secondary coil. One terminal of the secondary coil is connected to the bearing of a revolving drum coated with lampblack, the other terminal ending in a fine platinum point. The induced currents cause sparks from the platinum point which are recorded as tiny specks on the blackened surface of the drum. From the space between these specks and the speed of the drum, the time of detonation of the explosion train is found. The cartridges of the explosive are 3 cms. in diameter, and a total length of 3 to 4 metres is used, the cartridges being enclosed in an iron pipe and buried in sand.

The highest rate of detonation recorded in experiments with numerous explosives is about 8000 metres per second. A 4-metre length of explosive would therefore detonate in $\frac{1}{2000}$ of a second, and with a rotary speed of 25 metres per second the markings on the drum would be 12·5 mm. apart.

The velocity of detonation of explosives has been determined by Dautriche (Compt. rend. 1906, 143, 641), by a method depending on the use of detonating filaments, which had a constant and determined velocity of detonation of 6500 metres per second.

Two equal lengths of the filament are detonated, one of which is cut, and a tube filled with the explosive is interposed. One end of each filament is fixed to a detonating charge of fulminate, the other ends are bound together and fixed on a lead plate. The retardation of the velocity of detonation of the filament with the length of explosive introduced, causes the displacement of a depression mark on a sheet of lead from the position given when two equal uncut filaments are used. This displacement with the known velocity of detonation of the filaments give the time of detonation of the given length of the explosive.

Sensitiveness to percussion. The relative sensitiveness of explosives to direct blow is usually determined by finding the height at which a falling weight just fails to fire or explode them in one of several trials, and is frequently expressed in terms of the sensitiveness of an explosive of the same type taken as a standard, say picric acid for high explosives. Weights of different mass are used for explosives of different type[illegible] a 5-kilo weight being common for high explosives, in the form of a cylinder, with a plane striking face, and fitted at the sides with pulley wheels which run down vertical guiding rails. The explosive is spread evenly on the face of a heavy steel anvil, sometimes being covered with a steel disc, or the layer may be spread between two discs. With the less sensitive explosives a partial explosion or ignition occurs with a considerably less blow than that required to give complete detonation, and it is frequently difficult to say with certainty whether any decomposition has taken place or not. In these cases the limiting blow has to be fixed by a spark or faint flash, by smoke, or a stain on the anvil, or even the odour of decomposition products rather than by noise of explosion, and the results at the best are only approximate.

A sharper result is obtained with detonating explosives, and a more quantitative result can be obtained by the following method: the explosive in a very thin but continuous layer is placed on a dead-hardened and surfaced steel block and covered with a small steel cylindrical striker enlarged at the head and tapered at the base to give a circular striking surface, say, 0·2 inch in diameter, which is again dead-hardened and truly planed. This striker, which is pressed well down on the explosive, is held in a vertical position by means of a steel collar, in which the fit is good without offering any noticeable friction. The blow communicated through the striker is obtained by dropping a steel ball, falling freely and electrically released from a pointed magnet of just sufficient strength to support it, on to the centre of the top surface of the striker. The fall of the ball, the weight of which is selected according to the sensitiveness of the explosive, is determined by adjusting the electro-magnet fixed in a clamp working on a rod graduated in tenths of a foot. The shortest fall is determined, to one-tenth of a foot, which does cause ignition or explosion in at least one out of five attempts, and also the longest fall which does not cause ignition or explosion in each out of five successive attempts. From these falls the blows in foot-pounds per square inch are calculated, and a mean in round figures is recorded as the sensitiveness of the explosive. This method eliminates such influencing factors as friction of the pulley-wheels on the guides, the resistance of burred edges on the discs, and the blow of the falling weight not being truly given by the full striking surface, and it is only necessary to carefully adjust the layer of explosive to not only obtain concordant results, but also a quantitative idea of the blow required for ignition or explosion under the conditions of the test.

Detonator caps are tested by the fall, to a limiting height, of a small weight with a striking steel pointer.

Sensitiveness to friction. No satisfactory quantitative method of testing the sensitiveness of explosives to pure friction has been devised. One qualitative method is to rub the explosive between two surfaces of sand-paper fixed to a board and a sliding block of wood respectively, the latter being suitably weighted. This method is far from satisfactory; mercury fulminate, for instance, may frequently be reduced to fine powder by this means without firing.

The *sensitiveness to a glancing blow* is more usually taken as a measure of the comparative sensitiveness of explosives to friction, but this, again, can only be determined approximately. The method usually adopted, in which the personal factor is considerable, is to determine the number of ignitions or explosions obtained in a series of hard glancing blows with a box-wood mallet or steel hammer of given weight on a thin layer of the explosive spread out on a wooden floor, and on a stone and steel anvil alternatively.

As with sensitiveness to direct impact, the explosive must be at approximately normal temperature when tested, as the sensitiveness is increased with rise of temperature.

Sensitiveness to heat. The temperature of ignition of an explosive is very dependent on the conditions of the test. When slowly heated the ignition-point is lower than when the heat is suddenly applied, the heat of decomposition of the explosive causing its temperature to rise locally above the recorded temperature, to the ignition-point. The ignition-point should be taken as the temperature at which a not too small quantity, not less than 0·02 gram, ignites after it can reasonably be expected to have reached the recorded temperature, kept constant, say, after not longer than 5 seconds. The explosive is usually placed in a lightly covered thick glass tube immersed in a bath of air, oil, or fusible metal. Another useful form of apparatus is a long copper bar of square section in which two holes are drilled symmetrically with respect to the end of the bar, into which respectively a thermometer and small glass tube fit closely, so that the centre of the thermometer bulb and the bottom of the explosion tube are on a level with the axis of the bar. The temperature can be readily controlled by adjusting the size of the heating flame and its distance from the thermometer and explosion tube. The approximate temperature of ignition is first determined by gradually heating up the bath or bar until the explosive fires, and then the firing-point determined by trials with fresh quantities of explosive heated at definite temperatures, noting the lowest temperature at which explosion occurs under the conditions given.

Character and duration of flame. The photographing of the flame of explosives was first attempted by Schoeneweg, the inventor of securite, and is now very largely used in determining the character of the flames of mining explosives, propellants, and cap compositions.

In testing the flame of explosives, they are fired at night from a vertical steel cannon with a graduated scale placed behind it. The flame is photographed upon a drum covered with a sensitised film, rotating between screw pivots in a guide bracket, contained inside a box provided with a quartz camera lens for focussing the ultra-violet rays attending extreme heat. With the drum at rest, the length of the flame is obtained. To obtain the duration of the flame, the drum, which is motor-driven, is set in motion, and as soon as the required speed is obtained, the shot is fired electrically. From the speed of the drum and the lateral extension of the blurred image of the flame, the duration of the flame is obtained. According to Bichel, the limit values for the length of flame of a safety explosive lie between 0·4 and 2·24 metres, and the limit values for the duration of flame between $\frac{0\cdot28}{1000}$ and $\frac{10}{1000}$ of a second. Coal carbonite and blasting gelatin were taken as representing the two extremes.

Bichel compares the '*after-flame ratio*' of different explosives, that is, the ratio of the velocity of detonation, taken as unity, to the duration of the flame, as an indication of their safety. This ratio for coal carbonite is 1 : 8·7. and for blasting gelatin 1 : 883, so that Bichel concludes that the former is 100 times as safe as the latter. The flame of all explosives outlasts the time of detonation, but that of the safer explosives does so in much less degree than those of the less safe.

Ballistics of a propellant. So far as explosives are concerned, only the internal ballistics are meant when ballistics are referred to, that is, the phenomena which take place from the time ignition is brought about until the projectile is clear of the influence of the explosion gases. The ballistics concern principally the pressures developed in the gun and the muzzle velocity of the projectile. They can be calculated with some degree of accuracy for any particular gun, with any special nature and form of propellant, knowing the gravimetric density of loading, that is, the ratio of the volume of the powder to the capacity of the gun chamber, and the chemical composition and rate of burning of the powder. When explosion first takes place, the gun chamber may be looked upon as a closed vessel, so that the intensity of the initial chamber pressure and the rapidity with which it develops, depend directly on the loading density. The pressures obtained in a closed vessel are, however, never attained, owing to the motion of the projectile enlarging the chamber and lowering the gravimetric density.

In practice, the *pressures* attained in the bore of a gun are measured experimentally by means of crusher gauges, which are screwed into the bore of the gun at regular intervals, but in the ordinary proof testing of a propellant only the maximum chamber pressures are determined by means of a crusher gauge placed in the chamber. These crusher gauges have already been described in connection with the measurement of closed-vessel pressures.

In proving propellants, the *velocity* that a given charge will impart to a projectile in a particular gun, is determined by means of a Boulengé chronograph or some modification of this apparatus. The time taken by the projectile to pass over a known distance is determined in terms of the space passed through by a freely falling body in the same time. The projectile cuts through wires stretched on two frames a known distance apart. The cutting of the wire on the first frame liberates a rod suspended by an electro-magnet. The cutting of the wire on the second frame puts into action, by means of a second dropping rod falling through a shorter distance, a knife edge, which makes a nick in the first falling rod. From the space fallen through by the marked rod, the time for the projectile to pass over the distance between the two screens can be calculated.

In testing the ballistics of nitro propellants, they are heated to a definite temperature for some time before firing.

Bibliography.—A chronological bibliography on explosives up to the year 1895 will be found in the second volume of Guttmann's The Manufacture of Explosives.

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EXTRACTION APPARATUS. The object of extraction is to dissolve out some constituent or constituents from a substance by treating it with a solvent. When the substance is a solid it may be allowed to soak in the solvent at ordinary temperatures (*maceration*) or at higher temperatures (*digestion*), the solution being after a time poured off, both methods being included under the term *infusion*; a third method is to boil the substance with the solvent (*decoction*); and a fourth is to allow the solvent to descend through a column of the substance placed in a suitable vessel (*percolation* or *displacement*). The treatment when the substance is a liquid will be considered further on.

Solids.

Processes of extraction are involved in many of the large industries; for instance, in brewing; in the 'diffusion' process of obtaining sugar from sugar beet or sugar cane; in the 'lixiviation' employed in the manufacture of various inorganic salts, &c., &c.; and descriptions of them will be found elsewhere. Besides these, extraction apparatuses are employed in the laboratory of a small size for quantitative work, and on a larger scale for making various preparations; in the manufactory they are used for preparing medicinal extracts, alkaloids, dyestuffs, tanning materials, and volatile oils, and in removing oil from seeds and fat from bones. A mathematical discussion of the processes of extraction of solids, including cases of the *counter current* system, is given by Hawley in J. Ind. Eng. Chem. 1917, 9, 866; 1920, 12, 493. *See* also Lewis, on p. 110.

When water is the solvent employed, the operation may be conducted in a large pan made of copper or nickel or enamelled iron fixed in an outer jacket of iron, so that a space is left between the pan and the jacket through which steam can be made to circulate and heat the contents of the pan. Such pans are either fixed and have a pipe and tap at the bottom to draw off the solution, as shown in section (Fig. 1), or else they are movable about an axis (Fig. 2), so that the pan can be tilted and the solution poured off; in these, the axes on which the pan rotates are tubular to permit steam to enter and escape from the space between the pan and its iron jacket. When the infusion has been continued for a suitable time, and the liquid has been drained off, the residue

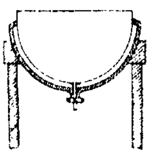

FIG. 1.

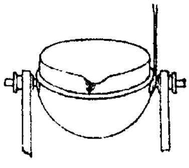

FIG. 2.

is placed in a canvas bag and subjected to strong pressure in a screw press, in order to squeeze out as far as possible the last portions of the solution. A common form of press consists of a base to which two uprights with a cross bar at top are fixed; in a thread cut through the centre of the cross bar works a powerful vertical screw. Between the uprights is a strong metal or wooden cylinder perforated with a number of holes; in this the bag of residue is placed, and on top is placed a thick plate which transfers the pressure exerted by the screw to the bag and its contents. The cylinder rests in a tray of a somewhat wider diameter, and provided with a spout; this tray collects and conducts off the expressed liquid to a vessel placed beneath the spout. Instead of pressing the residue, it may be infused several times more with water until it is completely exhausted of the desired constituents, but this method involves a large amount of subsequent evaporation. The solutions obtained by the above processes are next strained through conical bags of linen or flannel, and then evaporated down in jacketed pans like those previously described, the liquid being kept in motion by a mechanical stirrer.

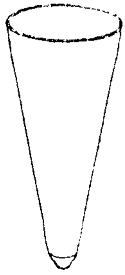

FIG. 3.

In many cases, evaporation at temperatures near 100° has an injurious effect on the substances in solution, and some arrangement for evaporation in a partial vacuum is adopted; this enables the evaporation to be conducted at a lower temperature than when the liquid is subjected to the pressure of the atmosphere.

In the process of *percolation* or *displacement*, the powdered substance is placed in a long cylindrical or conical vessel (Fig. 3), and rests on a perforated disc placed near the bottom and which can be covered with a piece of linen or flannel. A conical vessel is preferable to a cylindrical one, as the mass adjusts itself more readily to the vessel when any change of volume occurs; in a cylinder, if the mass swells on absorbing the solvent, it is apt to become so tightly packed that the liquid cannot pass, or, if it contracts owing to the removal of soluble constituents, it is more liable to form cracks and channels. A second perforated disc of linen or of paper pierced with holes is laid on top of the substance to distribute the solvent uniformly. It is often advisable to damp the powder with about half its volume of the solvent before packing it into the percolator, otherwise some portions may be found to have escaped getting wet during the whole operation. Care must be taken in packing that the substance is throughout in as uniform state of compression as possible, or else the solvent will pass more freely through the loosely packed portions. Different substances require to be packed with different degrees of tightness; and when alcohol or ether are the solvents employed, the packing may be tighter than in the case of water, as they do not cause such a swelling of the substance as water does. The conical vessel is supported in a circular hole cut in a table or wooden stand, a vessel is placed underneath to receive the solution, and the solvent is poured from time to time on the top. A row of such percolators can be arranged so that the solution from the first is poured on to the next and so on along the row, by which plan the liquid from the last will be a strong solution, and the percolators that are more nearly exhausted will receive the weaker and therefore more active liquids. This is a typical case of the *counter-current* system.

Glass percolators are also used consisting of an upper vessel to hold the substance and of a lower vessel to catch the solution. The upper vessel is stoppered to prevent loss of alcohol or ether vapour, but there must be a small aperture to allow air to enter in order to prevent a partial vacuum being formed. In extracting some plant materials cold percolation is found preferable to hot extraction as the desired constituent is obtained with less troublesome and undesired substances accompanying it and so is easier to purify.

For some purposes, more elaborate forms of aqueous extraction apparatus are preferable. Of these the following is an example:—

Hang and Reinhard's apparatus (Fig. 4).—This is designed for extracting dyewoods, &c., by the action of steam and water. A and B are two similar vessels (A is shown in section) which can be made to revolve about the axes *xy*, *xy*, by means of the gearing G, G, so as to facilitate filling and emptying. The axes are tubular and serve for conducting steam and water. In communication with the axis *x* are two pipes having taps *a′* and *a*; one ascends and leads into the upper part of the vessel, and the other descends, and, passing through the bottom of the vessel, leads to a perforated pipe, *g*, which forms a ring underneath a perforated false bottom, *h*. Communicating with the axis *y* is a pipe which descends and, following the dotted lines, joins on to the back of the three-way tap *b*. This tap *b* communicates with the space beneath the false bottom and also with the air. Another three-way tap, *c*, affords means of communication between the two axes *y*, *y*, and also with a pipe at the back indicated by the circle of dots. The covers of A and B can readily be taken off and fastened on again by the row of screws *s*, *s*, *s*, These covers form the condensing apparatus; inside they possess one or more flat horizontal coils *w*, *w*, to which water enters through the tube *m*, and escapes through *n*, and then flows over the whole lid, forming a layer on the top, and is thence conducted away. *e* and *f* are openings for air and safety valves, and *d*, *d*, *d* are taps for ascertaining the level of the liquid inside the vessel.

To work the apparatus A and B are filled with the substance to be extracted, and the covers are fastened on. A suitable quantity of hot water is introduced into A through the tap *c*, placed in such a position that it passes down the pipe *t* and through the tap *b* into A. Steam is now passed in through the axis *x*, and through the valve corresponding to *a*, and escapes through the perforations of the pipe *g*, heating the water and the substance and ascending to the top, where it is condensed and flows as liquid back to the bottom again. The action is further accelerated by opening the valve corresponding to *a′*, and passing steam in at the top of the apparatus.

The first few solutions, which are strong, are drawn off by the tap *b*, then the later and weaker ones are forced by the pressure of the steam into the vessel B, the taps *b* and *c* being placed so as to lead to that vessel. A is then emptied and refilled with fresh material, and B is now worked in the same way that A was. By proceeding in this way alternately with A and B, the later and weaker solutions from one vessel come into contact with fresh material in the other and become strong, and thus economy in evaporation is effected (D. R. P. 18922, 1881; and Dingl. poly J. 1882, 246, 22, a later form of that in D. R. P. 10771, 1880; and Dingl. poly. J. 1880, 238, 332).

In the laboratory most extractions are made with non-aqueous solvents, but those of tanning materials are made with water. For descriptions of the methods, *see* the article on **Leather**; and *see* Procter's Leather Industries Lab. Book of Anal. and Exp. Methods, 1908. Other references are: Wollny (Zeitsch. anal. Chem. 1885, 24, 50); Koch (Dingl. Poly. J. 1888, 267, 515); von Schroeder (Zeitsch. anal. Chem. 1886, 25, 132); Boegh (J. Soc Chem. Ind. 1899, 18, 303), comparative results with various apparatuses; Veitch (J. Amer. Chem. Soc. 1905, 27, 724; and 1906, 28, 505), recommends using water in adaptations of Zulkowski's or Soxhlet's apparatus; Rogers (*ibid.* 1906, 28, 194); Wilson (J. Soc. Chem. Ind. 1912, 31, 97) describes a form in which non-volatile solvents can be made to circulate over the material by means of a vacuum pump; Benson and Thompson (J. Ind. Eng. Chem. 1915, 7, 915).

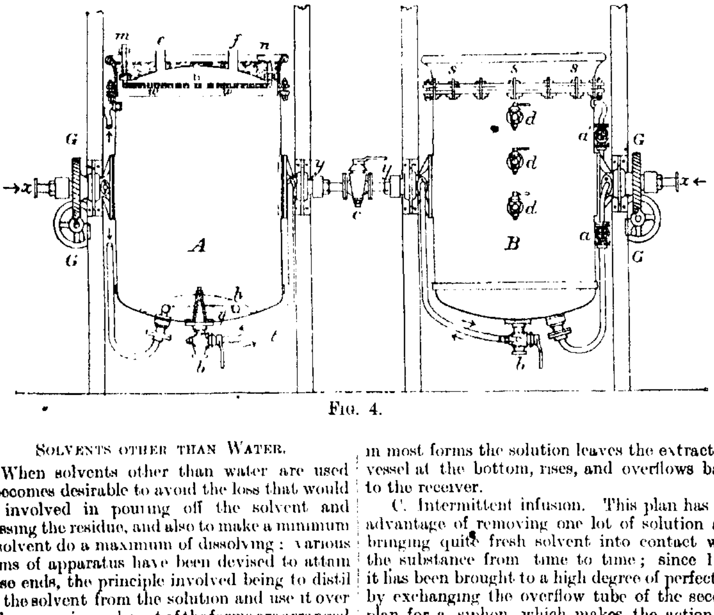

FIG. 4.

SOLVENTS OTHER THAN WATER.

When solvents other than water are used it becomes desirable to avoid the loss that would be involved in pouring off the solvent and pressing the residue, and also to make a minimum of solvent do a maximum of dissolving: various forms of apparatus have been devised to attain these ends, the principle involved being to distil off the solvent from the solution and use it over and over again, and most of the forms are arranged so as to work automatically and to require but little attention. In general, they consist of a receiver in which the solvent is boiled, and to which the solution of the extracted constituents returns, of an extraction vessel in which the substance is placed, and of a tube or space to conduct the vapour to a condenser, which cools and returns the liquefied solvent to the extraction vessel. If this tube is made to pass outside the extraction vessel, the extraction goes on in the cold, or nearly so; but if the vapour encircles the extraction vessel, or if the tube passes through the material, the solvent action is increased by heat which may or may not be desirable.

There are three main plans on which they are constructed, namely:—

A. Percolation.

B. Continuous infusion. In this plan the substance is always immersed in the solvent and in most forms the solution leaves the extraction vessel at the bottom, rises, and overflows back to the receiver.

C. Intermittent infusion. This plan has the advantage of removing one lot of solution and bringing quite fresh solvent into contact with the substance from time to time; since 1879 it has been brought to a high degree of perfection by exchanging the overflow tube of the second plan for a siphon, which makes the action an automatic one, the improvement being due to Soxhlet and Szombathy.

The number of forms for laboratory use that have been described in chemical journals, taking those for solids and liquids together, amounts to over 200. Some of them are triumphs of glass-blowing, but promise to be very fragile and difficult to clean, especially those designed for extracting liquids. Difficulties have been met in various ways. If corks are used for making junctions, there is the possibility of their yielding matter to the solvent, and a previous extraction with solvents may be required, which does not improve their qualities; if large, they have pores which allow the escape of some of the vapour. A covering of tinfoil is one remedy proposed, another is the use of chrome-gelatin recommended by Neumann (Ber. 1885, 18, 3064). The cork is smeared with a preparation made by dissolving 4 parts of gelatin in 52 parts of boiling water, filtering, and adding 1 part of ammonium dichromate, and is then exposed to light for 2 days, which renders the mixture insoluble in water, ether, and benzene. Another alternative is to use ground glass stoppers and joints, as in the apparatuses of Sanders, Jerwitz, von der Heide, and others; these are apt to jam and break. A third plan is to employ mercury seals, as in Schwarz's apparatus, and in Knorr's. It is much in favour in the United States. A simple way of making a mercury joint is given by Leather (J. Soc. Chem. Ind. 1889, 8, 81). When mercury is used, all minute globules of it must be carefully removed before weighing a vessel, as their weight is considerable.

To prevent portions of the substance being washed into the receiver, it is often necessary to enclose it in a cartridge of filter paper, or in a holder of filter paper shaped like a thimble; such thimbles are now manufactured for the purpose. Boeck (J. Ind. Eng. Chem. 1912, 4, 303) recommends a thimble made of alundum (that is bauxite fused in an electric furnace) fired with some suitable ceramic bonding material, it can be made as porous as desired. Forbes (*ibid.* 544) finds that alundum vessels alter a little in weight by varying treatment. Aluminium cups perforated at the bottom to hold the thimble or the substance directly, have been described (Richardson and Scherubel, *ibid.* 220; and Bersch, J. Soc. Chem. Ind 1901, 20, 389).

Various accessory devices have been added to the Soxhlet and other forms, the object of some being to divert at will the stream of condensed solvent from returning to the receiver and to collect it apart. In this way, at the end of an extraction, the solvent can be distilled off and recovered without disconnecting the apparatus. Such are those of Shenstone (Chem. Soc. Trans. 1883, 43, 123); Wollny (Zeitsch. anal. Chem. 1885, 24, 49); Fresenius-Offenbach (Zeitsch. angew. Chem. 1896, 485); Chatelan (Chem. Zeit. 1901, 25, 612); van Leeuwen (*ibid.* 1907, 31, 350); R. von der Heide (*ibid.* 1911, 35, 531); Friedrichs (J. Amer. Chem. Soc. 1912, 34, 1509; and Zeitsch. angew. Chem. 1912, 25, 2208). Further, a tap can be attached either to the bottom of the extraction vessel, or somewhere on the tubes, so that some of the solution can be drawn off for testing, as described by Lewkowitsch (Chem. Soc. Trans. 1889, 55, 359); Landsiedl (Chem. Zeit. 1902, 26, 274); Stein (*ibid.* 1909, 33, 1115); Taurke (*ibid.* 1912, 36, 214); Schmid (*ibid.* 1249). In order to lead ether down from the end of the condenser to the substance, Bain (J. Ind. Eng. Chem. 1910, 2, 455) employs a silk cord with a glass bob at the end; sealed in this bob is a piece of iron wire, so that by means of a magnet it can be drawn to the side to wash particles down. It is sometimes advantageous to attach a calcium chloride drying tube at the top of the condenser to prevent the ether absorbing water.

Below are given descriptions of well-known or typical apparatuses, and also references to other forms that have been described. Apparatuses suitable for the laboratory are taken first, and are, for the most part, grouped on the classification given above, then follow some examples of manufacturing plant.

A. *Percolation Forms.*

Zulkowski's apparatus (Fig. 5).—The substance is placed in the extraction vessel E, and is supported by a plug of cotton wool, *p*. The vapour of the solvent, as it boils off from the flask R, passes upwards through the side tube *t*, which is fused on to E, and then passes through the adaptor C to a condenser. The condensed liquid flows back and percolates through the substance in E, and drops again into R (Zeitsch. anal. Chem. 1873, 12, 303).

Maly (Annalen, 1875, 175, 80), Wolfbauer (Ber. der Versuchsstationen, Wien, 1878, 1), Weigelt (Repertorium der anal. Chem. 1881, 1, 7), and Fluckiger (Zeitsch. anal. Chem. 1882, 21, 467) have described apparatuses which resemble or else are modifications of that of Zulkowski.

Drechsel's apparatus (Fig. 6).—A folded filter, having double the usual number of folds, so that it may fit well to the sides of the vessel, is placed in the glass globe E, and on this paper the substance to be extracted is put. The solvent is placed in the flask R, which has a tube *t* fused into its side; on warming R the vapour ascending through *t* and through the tube *m*, which is held in contact with *t* by a cork and is fused on to the glass apparatus C, passes on to a reflux condenser connected with C by the tube *r*. The condensed liquid flows back into C, and is led by the tube *n* into the globe E where it falls on the substance, and after having percolated through it returns to R again (J. pr. Chem. 1877, 123, 350).

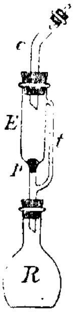

FIG. 5.

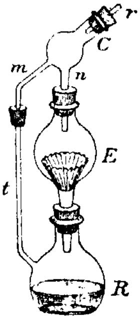

FIG 6.

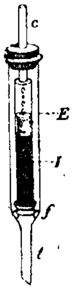

FIG. 7.

Weyl's apparatus (Zeitschrift für Instrumentenkunde, 1885, 5, 126) is an arrangement like Drechsel's, but by the employment of mercury joints an ordinary funnel can be used instead of the glass globe E.

Gwiggner's apparatus (Zeitsch. angew. Chem. 1902, 15, 882) consists of a vessel in which a funnel with the filter paper in position can be placed and the substance on the filter extracted by a volatile solvent. The vapour of the solvent rises between the funnel and the outer vessel, and when condensed drops from a ring of points on to the edge of the filter paper. It is useful for extracting sulphur from precipitates and in other analytical operations.

Tollens' apparatus (Fig. 7).—This is an improvement on an earlier form which was described by Tollens (Zeitsch. anal. Chem. 1875, [illegible]

The substance is placed in the inner tube I, which is slightly contracted at the bottom *f*, and then spread out into a rim over which a piece of filter paper is tied. This tube I is placed in a wider tube E, and rests on a bit of bent glass rod at *f*, which prevents it from closing the aperture into the narrower part *t*. The neck *t* is fitted by means of a cork into a flask containing the solvent, the vapour of which ascends through the space between I and E, and then through C to the condenser. The condensed liquid drops into I, and after percolating through the substance passes through the filter paper and back into the flask again (Zeitsch. anal. Chem. 1878, 17, 320). A form, having an extraction tube with a pointed lower extremity, is described by Dunstan and Short (Pharm. J. 1883, [3] 13, 663).

Schulze and von Rampach's apparatus resembles Tollens', with the exception that the inner tube I, in which the substance is placed, passes through and is held in its place by the cork at the top of the outer tube E The inner tube I is connected with a condenser, and is perforated just below the cork with one or more holes through which the vapour passes up to the condenser (Zeitsch. anal. Chem. 1878, 17, 171).

Scheibler's 1st apparatus (D R. P. 3573, 1878, and 7453, 1879; Dingl. poly. J. 1879, 234, 128), and also those of West-Knights (The Analyst, 1883, 8, 65) and of Bensemann (Repertorium der analytischen Chemie, 1886, 6, 390) differ but little from Schulze and von Rampach's.

Knorr's apparatus (Fig. 8).—This is much used in the United States, and was published by the Association of Official Agricultural Chemists. It avoids the use of corks and ground glass joints. R is a little flask made by softening the glass round about the neck of an ordinary flask and pressing the neck in so as to form a little depression. Resting on this neck by small projections *p*, there is placed either a tube E, with an internal siphon, or a simple percolating tube, ending below in a point, and having a perforated platinum disc sealed in near the point to support the substance. A long covering tube C (shown on half the scale of E and R) comes down over the percolator or siphon tube and fits into the depression in R the junction being made tight by a little mercury. R is held in position by an indiarubber band passing underneath it, and attached to the two projections *q*, *q*, on the covering tube. The latter is attached by fusion to the condenser, and the indiarubber stopper of the condenser is either put on before the fusion, or else is slit half way through, so that it can be put on later. *s* is a little siphon to remove any solvent that may collect between the cover and the flask neck. At the end of the extraction by means of an adapter fitting into the mercury joint the solvent can be distilled off and recovered (U.S.A. Dept. Agric. Chem. Division Bull. 28, 1890, 96; and Wiley's Princs. and Prac. of Agric. Anal. Vol. 3).

Variations of Knorr's form are given by Carr (J. Amer. Chem. Soc. 1894, 16, 868), Wheeler and Hartwell (*ibid.* 1901, 23, 338), Fraps (Amer. Chem. J. 1907, 37, 85), Dubois and Robison (J. Amer. Chem. Soc. 1908, 30, 797), Sy (J. Ind. Eng. Chem. 1909, 1, 314), Ames and Bowser (J. Amer. Chem. Soc. 1909, 31, 947), Francis (J. Ind. Eng. Chem. 1911, 3, 673).

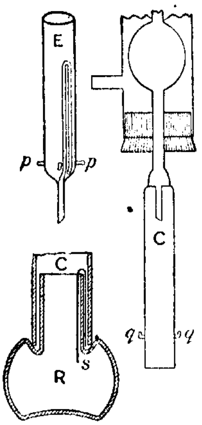

FIG. 8.

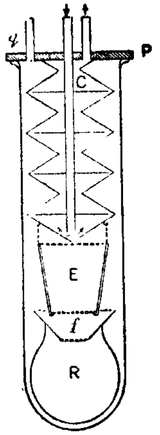

FIG. 9.

Wiley's apparatus (Fig. 9).—This is a compact apparatus used in the United States, it avoids all corks and joints. It consists of a large test-tube closed by the brass plate P, which has a ground undersurface resting on the ground edge of the test tube. Attached to P is the metallic condenser C, made of four sections, each formed of two cones fastened base to base; the cross plates shown are circular and direct the current of water against the sides. The substance resting on asbestos is contained in the crucible E, which has a removable perforated bottom, and hangs from hooks at the bottom of the condenser. The extract can either be collected and weighed in the test tube; or a little flask R, with a funnel *f* above it, can be used; in the latter case a little mercury is put in to fill the space between R and the test tube. The solvent is introduced by means of a small funnel through the tube *q*, which is closed when the solvent has boiled for a short time and has driven out the air (J. Anal. and App. Chem. 1893, 7, 65). The apparatus, and a way of arranging it in batteries, is given in Wiley's Princs. and Pract. of Agric. Anal. 1914, 3, 70.

The following are some other small apparatuses: West-Knights (Analyst, 1883, 8, 65); Thomas and Dugan (J. Amer. Chem. Soc. 1905, 27, 293), for removing bitumen from asphaltic mixtures; Jackson and Zanetti (Amer. Chem. J. 1907, 38, 461), a little percolating tube is placed in the flask of solvent and under the end of the condenser; Clacher (Analyst, 1910, 35, 349); Ford (J. Amer. Chem. Soc. 1912, 34, 552); Richardson and Scherubel (J. Ind. Eng. Chem. 1912, 4, 220); Cary-Curr and Cottle (*ibid.* 535 and 856), for testing rubber compounds used on wires; Walker and Bailey (*ibid.* 1914, 6, 497); Stokes (Analyst, 1914, 39, 295); Besson (Chem. Zeit. 1915, 39, 860).

One disadvantage in the percolation apparatus is that the drops from the condenser always fall on nearly the same spot of the surface of the substance, so that some portions do not get such a good chance of being extracted as others. To remedy this, Barbier (J. Pharm. Chim. 1878,

[4] 27, 200) employed an apparatus in which a siphon in a vessel above the percolator pours a considerable volume of the solvent from time to time on the substance, so that the surface of the latter becomes covered with a layer of liquid. The apparatuses of Guérin (J. Pharm. Chim. 1879, [4] 30, 511), Stockbridge (Chem. Centr. 1885, [3] 16, 280), and of Wollny are others that adopt this plan, and that of the last-mentioned is given below as a type of the class.

Wollny's apparatus (Fig. 10).—This consists of a receiving flask R to contain the solvent, and two other pieces shown in section in the figure. These bits are united together by the mercury joints *a*, *b*, *c*, *d*, which are provided with small tubes to permit of their being emptied without tilting the apparatus. The top joint *d* connects the apparatus with the condenser. The substance to be extracted is placed in the tube E; it should be contained in a cartridge of filter-paper so as to allow the vapour of the solvent to pass. The vapour ascends the tube *p*, and then passes downwards through E, heating the substance on its way, into the space F, whence it escapes up the tube *t* to the condenser. The condensed liquid collects in the vessel V, and is siphoned off from time to time by the tube *s*, thus ensuring the complete extraction of the substance. The solution returns through F and the long-tube *q* to the flask again. In cases where boiling the solution injures the dissolved constituents, vapour of the solvent can be introduced through the side tube *r* from another vessel of solvent heated separately, and the flask R can be left cold (Zeitsch. anal. Chem. 1885, 24, 48). Selecter (J. Ind. Eng. Chem. 1915, 7, 871) describes a modernised form on the same plan and less complicated than the above.

Von Bibra (von Gorup-Besanez's Anleitung zur zoo-chem. Analyse, 1850, 353) and Hoffmann (Zeitsch. anal. Chem. 1867, 6, 370), by alternately heating and cooling the receiving flask, make the solvent pass through the substance. Gawalowski (Zeitsch. anal. Chem. 1883, 22, 528) provides a tap on the side tube up which the vapour ascends, in a form like Zulkowski's; if this is closed from time to time, and the source of heat is removed, the contraction in the flask sucks the liquid back through the substance. He also employs underneath an arrangement like Drechsel's, whereby perfect filtration is attained.

Mohr's apparatus (Mohr's Lehrbuch der Pharm. Technik, 1847, 108) is an early form often referred to in older chemical literature; it employs a Woulfe's bottle with metal vessels above. Other old forms are those of Payen (Ann. Chim. 1845, [3] 13, 59); Schloesing (*ibid.* 1847, [3] 19, 239); Kopp (Comptes rendus des Travaux de Chimie par Laurent et Gerhardt, 1849, 5, 305); Arnaudon (Il Nuovo Cimento, 1858, 8, 200); Jacobi (Dingl. poly. J. 1862, 164, 343); and Storch (Zeitsch. anal. Chem. 1868, 7, 68), who constructs a simple form by placing the substance in a broken retort beak and embedding a tube in it through which the vapour of the solvent ascends to the condenser.

References to other authors who have described forms of percolation apparatus are: Vohl (Dingl. poly. J. 1871, 200, 236), for oil seeds; Gerber (Ber. 1876, 9, 656), for milk analysis; Cazeneuve and Caillol (J. Pharm. Chim. 1877, [4] 25, 265); Tschlapowitz (Zeitsch. anal. Chem. 1879, 18, 441); Biechele (Correspondenz-Blatt des Vereins analytischer Chemiker, 2, 70); Wolff (*ibid.* 91); Guichard and Damoiseau (Répertoire de Pharmacie, 1880, 8, 97); Gantter (Dingl. poly. J. 1880, 236, 221); Medicus (Zeitsch. anal. Chem. 1880, 19, 163); Thorn (D. R. P. 14523, 1880, and Dingl. poly. J. 1882, 243, 248; and with later improvements, D. R. P. 18850, 1881, and Dingl. poly. J. 1882, 246, 374); Dunstan and Short (Pharm. J. 1883, [3] 13, 663); Kreusler (Chem. Zeit. 1884, 8, 1323); Thresh (Pharm. J. 1884, [3] 15, 281); Will (*ibid.* 363); Waite (*ibid.* 376); Johnson (Chem. News, 1885, 52, 39 and 82); Foerster (Zeitsch. Anal. Chem. 1888, 27, 30 and 173); Neubauer (Dingl. poly. J. 1888, 267, 513; Berntrop (Zeitsch. angew. Chem. 1902, 15, 121), for bread analysis; Lohmann (Chem. Zeit. 1905, 29, 365); Peschoek (Zeitsch. angew. Chem. 1906, 19, 1513); Record (Chem. News, 1908, 97, 280); Gebhard and Thompson (*ibid.* 1909, 99, 124); Prager (Zeitsch. öffentl. Chem. 1909, 15, 396); Koch and Carr (J. Amer. Chem. Soc. 1909, 31, 1341); Lenz (Arbeiten Pharm. Inst. Univ. Berlin, 1909, 7, 289); Bornemann (Chem. Zeit. 1914, 38, 833), for fine powders, such as asphalt meal; Griffiths-Jones (Analyst, 1919, 44, 45), the tube up which the vapour ascends passes from the cork of the receiver up above the condenser, then bends over and passes down inside the condenser to the level of the water intake, the extraction thimble is attached to the condenser and is inside the receiver.

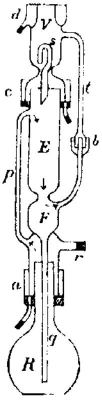

FIG. 10.

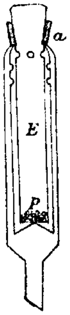

FIG. 11.

B. *Continuous Infusion Forms.*

Scheibler's 2nd apparatus (Fig. 11).—As the first apparatus could not be constructed wider to hold large quantities without danger of the solvent percolating in one channel through the substance, and leaving part unextracted, Scheibler designed a modification involving continuous infusion with an overflow. The apparatus (shown in section in the figure) is made of metal, and the substance is placed in the innermost tube E, which is closed at the bottom with a piece of wire gauze with a layer of cotton wool, *p*, above it. This tube slightly widens at the top and is ground into the top of the outer vessel so as to be removable. The outer vessel is composed of two tubes which are permanently united at the neck *a*; the outside one ends below in a funnel which fits into the vessel of solvent; the inner one is closed below, the bottom being bent up as shown; it has two rows of perforations in it near the top. The innermost tube has one row of perforations just below the neck. The vapour passes up the outer space and through the perforations to a condensor fitted to the neck of the innermost tube, the condensed liquid drops on to the substance, descends through it, then passes up the space between E and the next tube, and overflows through the lower row of perforations and so back into the vessel of solvent again (D. R. P. 9481, 1879).

Rempel's apparatus (Chem. Zeit. 1887, 11, 936) is also an overflow apparatus, but is so arranged that the substance is placed in the outside vessel and the liquid rises and overflows, and the vapour ascends through tubes in the centre.

Budde (J. Soc. Chem. Ind. 1914, 33, 184) found that when using heavy solvents to extract waxes or fats the solution is lighter than the solvent, and floats on the latter. He got over the difficulty by means of a tube something like E′ in Yoder's apparatus (Fig. 28), but in which the narrow side tube extends right up to the condenser and ends there in a funnel. In this way the column of heavy solvent in the side tube forces the light solution to overflow from the top of the wide part of E′ in which the substance is put. Caspari (*ibid.* 1913, 32, 1042) describes an apparatus for separating the pectous part of indiarubber by petroleum-ether; it would also meet Budde's difficulty.

Scheibler's 3rd apparatus (Fig. 12).—This was used in isolating vanillin from raw beetroot sugar. The substance to be extracted is placed in the vessel E (an elutriating vessel such as is used in the mechanical analysis of soils) and rests on a plug of cotton wool *b*. The solvent is poured on to it, until some escapes from the tube *t* into the flask R which is placed on a water-bath. The vapour of the solvent is conducted by the tube *p* back into E, whence it passes through *c* to a reflux condenser. The condensed liquid flows back through *c* on to the substance in E, thus causing a constant overflow of liquid from the end of *t*, carrying with it the soluble constituents of the substance, which thus accumulate in R (Ber. 1880, 13, 338*a*).

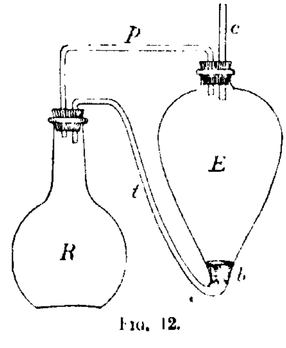

Fig. 12.

References to other continuous infusion apparatuses are: Wynter Blyth (Chem. Soc. Trans. 1880, 37, 140); Johnstone (The Analyst, 1885, 10, 81); Stoddart (*ibid.* 108); Schmidt and Hänisch (D. R. P. 42753, 1887; and Dingl. poly. J. 1888, 268, 564); Göckel (Zeitsch. angew. Chem. 1897, 683); Landsiedl (Chem. Zeit. 1902, 26, 274) for use with solvents of either high or low boiling-point; Warren (Chem. News, 1906, 93, 228), used in indiarubber works; Hahn (Chem. Zeit. 1913, 37, 880); Pinkus (Biochem. Zeitsch. 1914, 60, 311).

C. Intermittent Infusion Forms.

Auld and Pickle's apparatus (Fig. 13).—The substance to be extracted is placed, together with the solvent, in the large bolt-head flask E, which is heated in a water-bath. The vapour passes up the wide tube D, which is provided with a wide bore tap C, and is cooled by a reflux condenser attached to the top. *s* is a long tube ending in E in a small thistle funnel packed with cotton wool and covered with fine muslin or cotton cloth; the other end of *s* passes into the receiving flask R. A fairly wide tube, *t*, passes from the tube D at a point above the tap C down into the receiving flask R. When the solvent has become saturated, the tap C is closed for a moment, the pressure of the vapour then drives the solution through the cotton wool, and fills the tube *s*, which now acts as a siphon. The solvent is now boiled off from R, and passing up *t* is condensed and returned to E. The operation is repeated until the extraction is complete. With some solvents, a joint of wide indiarubber tubing can be used instead of the tap C, the tubing being pinched when it is desired to fill the siphon (Chem. News, 1909, 99, 242). The authors find that if the tube D is continued down into the flask E to a level a little above the thistle funnel, and is given a somewhat flanged termination, the apparatus will work automatically. When vapour is boiled off from E, it collects in D, forming a small column, which, when it has reached a certain height, forces the liquid into the siphon, which then empties E, and the process is repeated.

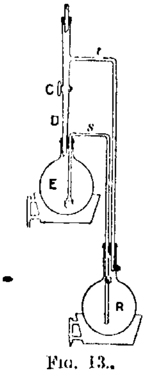

Fig. 13.

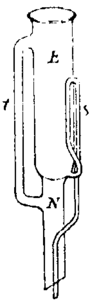

Fig. 14.

Schwaerzler (J. Pharm. Chim. 1853, [3] 24, 134), Schiel (Annalen, 1858, 105, 257), and Simon (Zeitsch. anal. Chem. 1873, 12, 179) have also described apparatuses in which the pressure of heated vapour is used to force the solution from one vessel to another.

References to other apparatuses of the intermittent infusion group are: Daubrawa (Vierteljahrschrift für practische Pharmacie, 1859, 8, 36); Fleury (J. Pharm. Chim. 1862, [3] 41, 282); Barlow (Chem. News, 1888, 57, 56).

Soxhlet and Szombathy's apparatus (Fig. 14).—This was the first apparatus to introduce the use of the siphon to effect automatic intermittent infusion. The substance to be extracted, contained in a cartridge of filter paper, is placed in the wide tube E, at the bottom of which a tube, *s*, bent so as to form a siphon, is fused on. Another tube, N, not quite so wide as E, is fused on to the bottom of the latter, without, however, opening into it. The down tube of the siphon *s* passes through the side of N, and is sealed in by fusion. A reflux condenser is fitted to the top of E, and the tube N is fixed by a cork into a vessel of the solvent. On boiling the solvent, the vapour ascends through N and through the side tube *t*, which is sealed into both N and E, and reaches the condenser, whence the condensed liquid drops back into E and accumulates until it rises to the level of the top of the siphon *s*, when the siphon flows and empties the liquid contents of E into the vessel beneath; E then fills again, and its liquid contents are siphoned off every time the level reaches the top of the siphon tube. The top of the cartridge should be below the level of the top of the siphon, so that it may be completely immersed in the solvent, and it should rest on a plug of glass wool or strip of metal bent into a ring so that the opening to the siphon may not be closed (Dingl. poly. J. 1879, 232, 461).

Soxhlet and Szombathy's plan is now very widely adopted, and many variations of it have been devised. Lewkowitsch (Chem. Soc. Trans. 1889, 55, 359) attaches a tap to the siphon just before it enters the tube N in Fig. 14, so that a little of the solution can be drawn off to test the progress of the extraction. The siphon may be placed between the extraction vessel E and an outer vessel or inside the extraction vessel; the risk of breakage is thus diminished, and the material and solvent are warmed by the ascending vapour. The following are references and descriptions of various forms having the siphon all, or mostly, in the air: Wollny (Zeitsch. anal. Chem. 1885, 24, 51); Boessneck's 2nd apparatus (Chem. Zeit. 1890, 14, 870); Christ Kob & Co. (*ibid.* 1901, 25, 379), a form having a perforated glass plate fused in position just above the place where the siphon is attached to E in Fig. 14; Landsiedl (Chem. Zeit. 1902, 26, 274) forms with movable interior vessels; Silberrad (Chem. News, 1911, 104, 54), like Fig. 14, but the main tube E rises very high and contains a pendent condenser; Kardos and Schiller (Chem. Zeit. 1913, 37, 920), for powdery materials, the solvent drops into a central tube full of holes and covered with cloth and embedded in the powder, whence it passes into the powder; Freund (*ibid.* 1914, 38, 802), a clever form easily made from common apparatus.

Clausnizer and Wollny's apparatus (Fig. 15).—In this, the bottom of the inner tube E is drawn out, and to it a siphon tube is sealed on, as shown in the figure. The tube E and its siphon fit loosely into an outer tube, T, which is fitted into a vessel of the solvent below and leads to a condenser above. The substance to be extracted is placed in E, and the mode of working is similar to that of the previous apparatus. The vapour passing up in the space between E and T maintains the substance and the solvent at a temperature approaching the boiling-point of the latter (Zeitsch. anal. Chem. 1881, 20, 81).

An objection to this form raised by Wollny is that as the siphon is in the hot vapour the solvent in it may boil and hinder the siphoning action, and he describes forms in which the substance is heated yet the siphon is cool (Zeitsch. anal. Chem. 1885, 24, 48). When the solvent is a mixture of liquids of different boiling-points, such as petroleum-ether, the more volatile portions tend to collect and boil in the extraction vessel, while the siphon is superheated by the vapours of the high boiling portions and does not act (Ford, J. Amer. Chem. Soc. 1912, 34, 552).

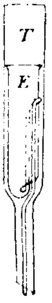

FIG. 15.

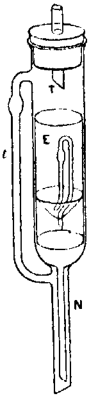

FIG. 16.

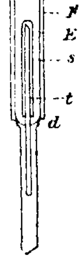

FIG. 17.

Frühling's apparatus (Fig. 16).—A cylindrical tube, E, resembling a tube for drying filters, is open at the bottom, but a little above the bottom it is closed by a conical diaphragm, through the apex of which passes the longer leg of a little siphon, which is thus held in position in E; it lies close to the side. This tube contains the material to be extracted, held in filter paper. The end of the siphon does not quite reach to the bottom of E, so that E can be placed upright on the balance pan, and weighed; it can be closed with a ground-in stopper during weighing. E is slipped into the outer tube T, which is closed by a light hollow glass stopper through which runs the tube of the condenser. The vapour of the solvent passes up the side tube *t*, is condensed, and the liquid when siphoned from E returns down the narrow tube in the interior of N (Zeitsch. angew. Chem. 1889, 242). Somewhat similar is an arrangement of Bain (J. Ind. Eng. Chem. 1910, 2, 455), he uses as a percolator a little weighing bottle which can be closed by ground-on caps at each end; in one end is a short movable glass inset carrying a stretched filter-paper on which the substance rests.

The feature of having the siphon inside the apparatus is adopted in the following forms: Blount (Analyst, 1888, 13, 126); Fresenius-Offenbach (Zeitsch. angew. Chem. 1896, 485); Sinnhold (Chem. Zeit. 1901, 25, 423); in this the vapour passes up a tube in the centre of a globular extraction vessel terminating below in a wide tube. The inner tube is ground into the wide tube, and has the siphon fused into it with the long leg passing down the centre, the bend and short leg being in the globular vessel. The apparatus is less fragile than other forms, and the inner tube and siphon can be removed in one piece for cleaning. Chatelan (Chem. Zeit. 1901, 25, 612) bends the delivery tube of the condenser slightly to one side, so that by twisting the condenser round, the solvent can be made to fall either on the material or into the orifice of a tube passing through the side of the extraction vessel near the top. When in the latter position, the solvent is run off through a tap on the side tube, and the necessity is avoided of disconnecting the receiving flask and distilling off the solvent in a separate apparatus. Landsiedl (Chem. Zeit. 1902, 26, 275) describes forms with movable interior vessels for hot extraction. Radermacher (*ibid.* 1177). Hesse (*ibid.* 1904, 28, 18) uses a cork in a tubulure at the bottom of the inner tube to hold the siphon in its place, thus making a very cheap form; the cork can be coated with chromgelatin. Pescheck (Zeitsch. angew. Chem. 1906, 19, 1513), a form with movable interior vessels for percolation or intermittent infusion. Vigreux (Bull. Soc. Chim. 1909, [4] 5, 699). Walpole (Chem. News, 1910, 102, 129), a form somewhat resembling Knorr's (Fig. 8). Aron (Biochem. Zeitsch. 1913, 50, 386). Beadle and Stevens (Analyst, 1913, 38, 143), a compact form made out of an Erlenmayer flask with a long neck holding a pendent condenser. Thar (Biochem. Zeitsch. 1914, 58, 503). Twiss and McCowan (J. Soc. Chem. Ind. 1917, 36, 692), a form much like Blount's.

King's apparatus (Fig. 17).—In this the siphon is differently constructed. Into the bottom of the wide tube E there is fused the long narrow tube *t*, which is ground off at an angle at its upper end. A tube, *s*, slightly wider than *t*, and closed at one end, is inverted over *t*, and rests on the upper end of the latter: it does not quite reach to the bottom of E. The tube E slips into a still wider one, F, which is dented in in several places at *d*, in order that the dents may support E and prevent it closing the narrower part of F. The substance to be extracted is placed in E, and rests on a plug of glass wool at the bottom. It is fitted up as in the two previous apparatuses, and when the liquid in E rises to the top of *s*, *s* and *t* form a siphon and draw off the liquid into the vessel below (Chem. News, 1888, 57, 235). Masojidek (Zeitschrift für Zuckerindustrie in Böhmen, 1881, 6, 51) and Boessneck (Chem. Zeit. 1887, 11, 1600) had previously described apparatuses on the same plan as King's. Thorpe and Robinson (Chem. Soc. Trans. 1890, 57, 44) employ an open-topped bell-jar inverted with a siphon of this form to make a capacious apparatus.

In Jerwitz's apparatus and in Sanders's apparatus, the difficulty of the cork is avoided by causing the condensed solvent to enter the extraction vessel at the side instead of at the top; a light glass stopper can then be used to close the top of the extraction vessel, and the material undergoing extraction can easily be removed when extraction is complete, and fresh material introduced without disconnecting the condenser.

Jerwitz's apparatus (Fig. 18).—In using this the receiving flask F is attached to the bottom of the condenser and is held on by spiral springs. The cartridge of material to be extracted is placed in the extraction vessel A; ether is poured in up to the level E, and the vessel is closed by the glass stopper H, which is held in position by spiral springs. The tap B is then opened, and the ether is siphoned over into F. On heating F in a water-bath, the ether vapour ascends to K, and is there cooled by a current of water circulating in the outer space. The condensed ether is prevented by the projecting tube J from flowing straight down into F, and is conducted through L into A, where it collects and is siphoned off intermittently through G. When the extraction is complete, the stopcock B is closed and the ether from F is driven off and collected in A. F is then removed, B is opened, and the ether is siphoned off into another vessel. The stopper H is then removed, and the cartridge of exhausted material is taken out by long tongs or a wire hook. At the top of the apparatus, a calcium chloride tube, O, prevents access of moisture to the ether, and the little tube D containing mercury and a plug of cotton wool acts as a safety valve should O get clogged (Chem. News, 1901, 83, 229).

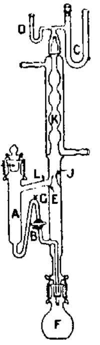

Fig. 18.

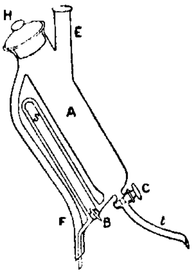

Fig. 19.

Sanders's apparatus (Fig. 19).—In this apparatus, the material is placed in the extraction vessel A, which is closed by the glass stopper H and is held in a sloping position. The receiving flask containing the solvent is attached to the tube F, the taps B and C are closed, and on heating the flask, the vapour of the solvent passes up the tube F and through the upper part of A to the side tube E, which leads to a reflux condenser. When A is nearly filled with the condensed solvent, the siphon *s* discharges the solution into the receiving flask, and continues to work intermittently as in similar apparatuses. When the extraction is complete, the tap C is opened and the solvent is collected at the end of the tube *t*. If the tap B is left open during the operation, continuous percolation instead of intermittent infusion is effected. In a simpler form, the tap B and the cross connection between the legs of the siphon are absent. The apparatus can be made on a large scale of tinned copper, the extracting vessel having the capacity of one litre (Chem. Soc. Proc. 1910, 26, 227).

When oil seed is crushed for analysis some of the oil is lost in the machine. Max Lehmann (Chem. Zeit. 1894, 18, 412), to meet the difficulty, designed a very small mill in which 5 grams can be crushed, and then the lower part of it containing the meal can be put in a Soxhlet for extraction. Another uncommon apparatus is that of C. Lehmann (Pflüger's Archiv Physiol. 1903, 97, 419 and 606) for extracting the fat from animal tissues, yeast, &c.; it is composed of a bottle with stoppered mouths at top and bottom, in which the substance is placed, together with the solvent and a number of porcelain balls. This is rotated in a motor, and is then made to form part of a Soxhlet apparatus.

Large Forms.

Apparatuses designed to deal with several pounds of substance are described by: Thorpe and Robinson (Chem. Soc. Trans. 1890, 57, 41), to hold 14 lbs. of bark; Buss (Chem. Zeit. 1903, 27, 813), for the hot extraction of several kilograms: Jackson and Clarke (Amer. Chem. J. 1909, 42, 287), for 18 kilograms of turmeric; Roberts (*ibid.* 1910, 43, 418), a battery of cells in series for charges of 3 kilograms of corn meal; Hallo (Biochem. Zeitsch. 1911, 36, 245), to hold 2 kilograms; Schmidt (J. Ind. Eng. Chem. 1916, 8, 165), to remove fat from several pounds; McNair (*ibid.* 838), it resembles a Wiley's apparatus (Fig. 9) made on a very large scale, with a bucket in place of the crucible; Schwalbe and Schulz (Chem. Zeit. 1918, 42, 194), for 4 to 6 litres of material.

Manufacturing Forms.

Roth's apparatus (Figs. 20 and 21).—This is employed for extracting oil from seeds by means of carbon disulphide. The solvent is stored in a reservoir, which is kept immersed in water to check evaporation. A pipe from an elevated water reservoir enters at the top of the carbon disulphide reservoir, and another pipe communicating with the extractor passes through the top of the reservoir and descends nearly to the bottom; so that when the tap of the water pipe is opened, the carbon disulphide is forced into the extractor. The latter is a cylindrical vessel, shown in section in Fig. 20; it is provided with a perforated false bottom, F, supported by struts G, G. The false bottom F is covered with sackcloth, and on it the ground seed or oil cake is placed and filled in up to another perforated plate, J, also covered with sackcloth. The top of the extractor is fastened on with screw clamps so as to be readily removable. At the bottom is a T-piece, communicating by the opening B with the carbon disulphide reservoir and, by the branch C, with a steam boiler. When filled and closed, carbon disulphide is forced in through B, and when it has dissolved the oil, fresh carbon disulphide is forced in at B, causing the first charge to overflow down the pipe L, the entrance to which is protected with a strainer, and to pass to the distilling apparatus. A gauge, Q, shows the level of the liquid, and also allows samples to be drawn. The material is treated some three times or so with the fresh solvent until a sample taken at Q is found to be free from oil; half of the last charge is then conducted through the tap E, and a pipe connected with it to another similar extractor, and the other half is returned to the carbon disulphide reservoir. In order to recover the last portions of solvent adhering to the material, the valve N is opened and steam is sent in through C; the carbon disulphide is thus boiled off and passes through N to a

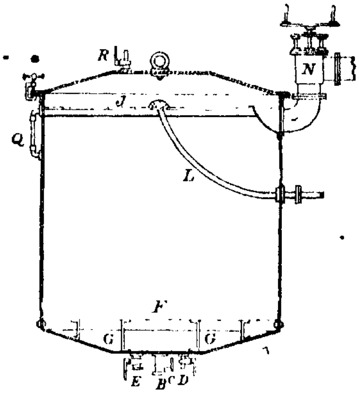

FIG. 20.

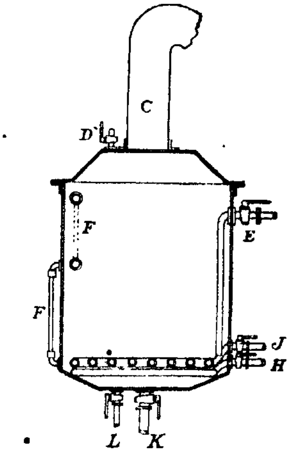

FIG. 21.

condenser. When all carbon disulphide is driven off, the taps R and D are opened; the former allows the steam to escape and the latter allows the condensed water to run off. The cover is then removed and the extractor is emptied and refilled with fresh material.

The distilling apparatus, shown in section in Fig. 21, is a cylindrical vessel, into which the solution of oil is introduced through the tap E and pipe attached which descends nearly to the bottom. The vessel is half filled with liquid, the level being ascertained by the gauges, F, F. At the bottom of the vessel are two steam coils; the lower one is perforated with a number of small holes and is fed by the tap H; the upper one is not perforated, and is fed by the tap J, and the condensed water from it escapes through the tap L. At first, steam is slowly passed through the upper coil and heats the carbon disulphide, the vapours of which pass by the wide tube C to a special form of condenser; when nearly all the carbon disulphide has escaped, steam is passed through H, and, escaping by the perforations through the oil, removes the last traces of the solvent. The tap D allows the steam to escape at the end of the distillation. The oil is finally run off through the tap K to a reservoir, where it is allowed to stand until the condensed water has separated in a layer (Schaedler's Technologie der Fette und Oele, 1883, i. 292).

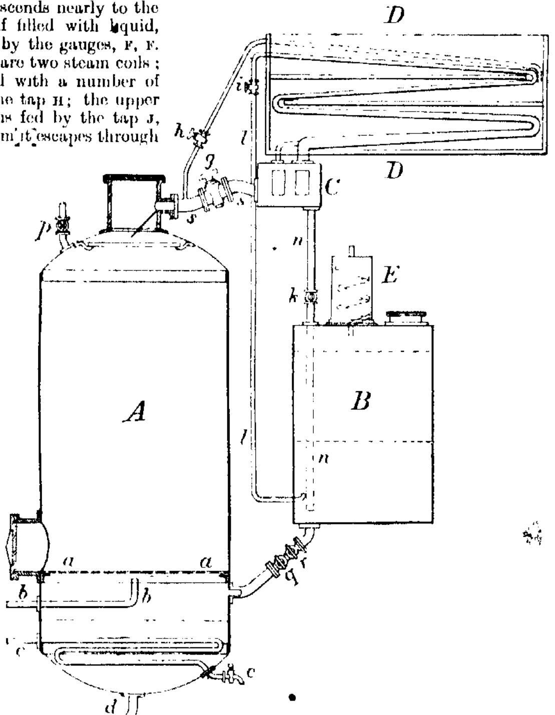

Fig. 22

Leuner's apparatus (Fig. 22).—This is employed for removing fat from bones. The bones are filled into the cylindrical vessel A (shown in section in the figure), and rest on the perforated false bottom *aa*; then all the taps are closed except *p*, and steam is injected through the pipe *b*; when all the air is expelled, *p* is closed, and the bones are kept in contact with steam under pressure for a time. Steam is then shut off, and the taps *p* and one attached to the tube *d* are opened, and the condensed water is drawn off. In the cylindrical vessel B there are placed equal volumes of water and petroleum naphtha or other volatile solvent: taps *p* and *d* are closed, and taps *g* and *i* are opened, as also are the taps *q* and *r*, to allow the water and solvent to flow into A; *q* and *r* are then closed, and an equal volume of water is introduced into B. Steam is now passed through the pipe *cc*, and this heats the water which forms the lower layer in A, and the heat is communicated to the upper layer of solvent. The vapour rises through the bones and passes through the pipe *ss* to the small vessel C, and thence to the reflux condenser contained in D. The condensed liquid collects in C until it reaches the opening into *s*, when it flows back into A and is spread over the bones by the arrangement shown at the top. Any vapour that is not condensed passes through the pipe *l*, and is led under the surface of the water in B, which is provided with a small condenser E to prevent the escape of vapour of the solvent to the air. The bones are thus subjected at the same time to the action of steam and petroleum vapour and also of liquid petroleum. After this action has gone on for some time, the tap *g* is closed and *h* is opened; the vapour evolved from A then passes to a second condenser, which is contained in D and communicates with C—it is indicated by dotted lines—and the tap *k* is opened; this allows the solvent to flow from C down the tube *nn* and collect in B. The heating is continued until all the solvent is driven off and water only enters C; this can be seen by glazed apertures in that vessel. When this occurs, the operation is finished, and a mixture of fat and of aqueous liquid is drawn off by the pipe *d*, and the latter is used in preparing glue (D. R. P. 17181, 1881; and J. Soc. Chem. Ind. 1882, 1. 155).

Merz's apparatus (Fig. 23).—This apparatus is designed for the extraction of various substances with volatile solvents; it can also be used with animal charcoal for decolourising purposes. It consists of an inner vessel, E, which is open at the top and is contained in a closed outer vessel R. The substance is filled into E through the manhole *a*, and at the end of the operation it is removed through the manhole *b*. The solvent is stored in a reservoir S, which forms the lower part of the condensing vessel T, and is divided from the upper part by the partition *d*. The extractor E is filled with solvent by opening the tap *t*. When the level of the liquid rises as high as the top of the siphon *s*, the latter begins to act and runs off the liquid from E into the outer vessel R. The entrance to the siphon is protected by the sieve arrangement shown at the bottom of E. Steam is made to circulate through the coil *ee* at the bottom of R; this causes the solvent to boil, and its vapour circulates in the space between R and E, warming the latter and its contents, and then passes to the condensing tubes *c*, *c*, *c*, round which water is circulating. The condensed liquid falls back into E, and when the level again reaches that of the top of the siphon the siphoning-off is repeated and so on over and over again. The substance is thus submitted to intermittent infusion. Samples can be drawn off at *u*, and when the extraction is found to be complete, the water that surrounds the tubes *c*, *c*, *c* is withdrawn. The solvent then boils off, and after condensation in the worm W returns to the reservoir S. The extract is drawn off by the tap *v*. By regulating the tap *u*, the substance can be made to undergo continuous instead of intermittent infusion, if desired (D. R. P. 20742, 1882; and J. Soc. Chem. Ind. 1883, 2, 234).

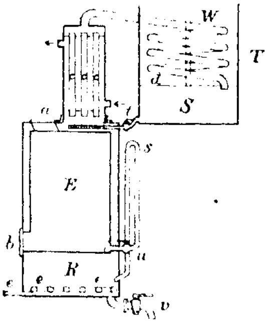

FIG. 23.

Van Urk (Pharm. Weekblad, 1919, 56, 1301) describes a simple apparatus.

See also the article on OILS, and Ubbelohde's Handbuch der Chemie und Technologie der Öle und Fette, 1908, i. 574, &c., where the extraction of oils on the manufacturing scale is dealt with at some length.

The extraction of the volatile oils to which the odour of flowers is due, forms an important industry; the apparatus employed is simple in principle, the only complexity being in the arrangement of the battery of extracting vessels, reservoirs of solvent, and stills (*see* Gildemeister, Die Ätherischen Öle, 2d. ed. 1910, 266).

Garnier's apparatus (Figs. 24, 25, and 26), however, presents some novelty; it consists of a cylinder, C, revolving on a horizontal axis inside a cylindrical vessel, V; the end plates E, E of the revolving cylinder present a number of circular rings (Fig. 25), each of which is united to the corresponding ring at the other end by a number of rods forming an open framework (Fig. 26). Into the frames formed by the rods long cylindrical baskets B, B of open work containing the flowers can be thrust through a manhole, M, at the end of the cylindrical vessel. When all the baskets are in position, the manhole is closed, and enough solvent is introduced through F to cover the lowest basket. The cylinder is then made to revolve, and thus one basket of flowers after another is immersed in the solvent; as the cylinder has no outer wall, the solvent can move freely through the baskets. Heat can be applied by passing steam through the spiral pipe PP, and the vapours of the solvent pass by the still head S to the condenser K. When extraction is complete, the solution is drawn off by the tap T. At the end of the operation, steam can be blown into the apparatus through the tap U, and the last remnants of the solvent can thus be driven off and condensed in K. By this apparatus, many baskets of flowers can be extracted by the same comparatively small quantity of solvent (Fr. Pat. 1904, 342534; Gildemeister, *l.c.* 271).

Extraction plant, solvents and methods on the manufacturing scale are discussed by Pooley in The Chemical Age, 1920, 2, 121.

Liquids.

A substance held in solution or suspension by a liquid can often be removed by treating the liquid with a solvent that is not miscible with it. In the rest of this article 'liquid' will always be used to denote the liquid submitted to extraction.

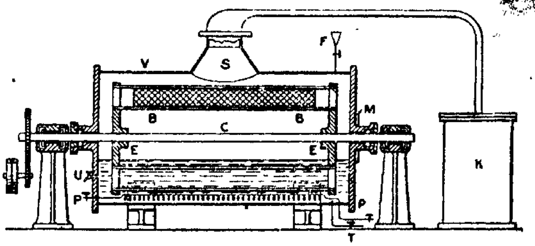

FIG. 24.

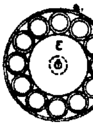

FIG. 25.

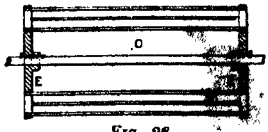

FIG. 26.

The ordinary procedure is to shake the liquid and the solvent vigorously together in a separator, which is a pear-shaped or cylindrical glass vessel terminating in a stoppered tubulure at its broad or top end, and in a stopcock and short tube at its narrow or lower end. After shaking, the vessel is allowed to stand until the liquid and the solvent have separated into two layers. The stopper is then removed, and the lowermost layer tapped off by means of the stopcock and tube. This treatment is repeated with fresh solvent until the liquid has given up as much as possible of the dissolved or suspended substance it contained

The mathematical aspect of the process is discussed by Marden and Elliott (J. Ind. Eng. Chem. 1914, 6, 315 and 928), and they give the formulæ—

$$\text{(i)}\ x_n = x_0\left(\frac{da}{c+da}\right)^n;\quad \text{(ii)}\ d = \frac{C_1}{C_2};$$

where a is the volume of the aqueous solution containing the substance; c is the volume of the solvent used to extract it, the same volume of fresh solvent being used for each extraction; x_0 is the concentration in the aqueous liquid (that is, the amount of substance in unit volume) before commencing the extraction; x_n is the concentration in the aqueous liquid after n extractions; C_1 is the concentration in unit volume of the aqueous liquid after an extraction; and C_2 is the concentration in the same volume of the solvent after the extraction. The law of distribution of a substance between two immiscible solvents states that after shaking until equilibrium is established, the value of d, the distribution ratio, as defined above, is constant for a given temperature, irrespective of the amounts of substance present, provided the substance does not polymerise. The law does not hold good, however, for wide variations in concentration, and corrections must be made for the amounts that the solvents dissolve of each other. From the equations it follows that the smaller d is, the fewer extractions will be required to reduce the amount of substance left in the aqueous solution to an unimportant quantity; and if d is known, the number of extractions required to attain this can be calculated. The authors have determined d in the case of the alkaloids and of some other substances. Another mathematical discussion of the subject but for solids and gases is given in Lewis's Principles of Counter Current Extraction (J. Ind. Eng. Chem. 1916, 8, 825). Pinnow (Zeitsch. Nahr. Genussm. 1919, 37, 49) has investigated the extraction by ether and the distribution coefficients between ether and water of various organic acids.

Various forms of apparatus have been devised to effect the extraction by automatic processes similar to those employed for solids. Two different cases arise: one when the solvent is heavier than the liquid, and the other when it is lighter. In the first case, the heavier solvent must pass as a rain of drops through the liquid and escape up a side tube when a certain amount has collected, the column of liquid balancing a shorter column of solvent in the side tube. In the second case, a column of the solvent must be caused to accumulate in a tube until it acquires sufficient pressure for some to escape at the bottom and pass up through the liquid. It is important that the apparatus be so designed as to allow a column of sufficient height to collect.

A third plan is to boil the solvent and force the vapour through the liquid; for this great efficiency is claimed, but it obviously requires great care in adjusting the apparatus and rate of working to the particular liquid and solvent, and the sucking back of the liquid into the boiling vessel when the latter cools has to be guarded against. A cooling worm, through which a current of water flows, is usually immersed in the liquid so as to help condense the vapour of the solvent and control the temperature.

The name 'perforation' has been used for all three plans by some writers, but it is not at all appropriate, as they are not processes of making holes. *Perpluviation* would be more suitable for the first two, and *injection* for the third.

Various practical points have to be attended to: thus regular boiling in the receiving vessel must be ensured by means of fragments of clay pipe, or one of the usual devices. When a heavy solvent is used some should first be poured into the extraction vessel before adding the liquid so as to prevent any of the latter entering the side tube. A tendency of the liquid and solvent to form an emulsion is apt to cause difficulties in carrying out the extraction When this happens various plans can be tried, such as allowing time for the liquid and solvent to separate, or gentle warming, or dilution of the liquid. Wollny (Zeitsch. anal. Chem. 1885, 24, 53) says that at a boiling temperature an emulsion is less likely to form. If an obstinate emulsion has formed, sucking through a fine-pored or hardened filter, or rotating in a centrifugal apparatus, can be tried to effect a separation. Some authors state, however, that warmth promotes emulsification. Self (Pharm. J. 1915, 95, 164) discusses the merits of various solvents as extracting agents and methods of dealing with emulsification. He recommends shaking with more of the solvent as the best way of breaking an emulsion. Malfatti (Zeitsch. anal. Chem. 1898, 37, 374), dealing with urine, which is prone to form emulsions, makes it descend a spiral of woollen thread wound round a long central tube placed in an outer tube up which ether ascends.

Kempf (Chem. Zeit. 1910, 34, 1365; and in Abderhalden's Handbuch Biochem. Arbeitsmethoden) gives the following points of importance in the practical working of extraction by ether: (A) In arranging for the heights of the liquid and of the column of ether allowance must be made for the increases in volume and changes in relative density due to (*a*) expansion by rise of temperature; (*b*) the liquid dissolving some ether and so increasing in volume it may be as much as 10 p.c.; (*c*) the liquid in the funnel tube at the start being pushed down and so raising the level of the liquid in the extraction vessel; (*d*) the drops of ether rising through the liquid also adding to the rise of level. (B) The ether will dissolve a certain amount of water and transfer it to the receiver; ether can also dissolve and transfer a small amount of sulphuric acid from a liquid containing it. (C) If the ether boils slowly the effect of a fractionating apparatus is produced, and water accumulates in the receiver and may separate as a layer. Rapid boiling of the ether diminishes this accumulation as water vapour then accompanies that of the ether. (D) The ether should be as pure as possible, especially for extracting fat or aliphatic acids or compounds easily acted on. Commercial ether, especially if it has been long exposed to light, is apt to contain H_2O_2 and organic peroxides, alcohol, aldehydes, and acids. The alcohol would make esters with strong organic acids, and the peroxides would resinify easily oxidisable substances; they have even been known to detonate when the solution was evaporated. If the extraction is lengthy it is well to carry it on in a dark room to diminish oxidation. Tcherniac (Chem. Soc Trans. 1919, 115, 1092) suggests saturating an aqueous liquid with sodium chloride to diminish the loss of ether caused by some being dissolved.

The forms of apparatus may be grouped into those for small quantities of liquid in which the extraction vessel is placed vertically over the receiver in which the solvent is boiled and to which the solution returns, and those for larger quantities in which the receiver is situated alongside the extraction vessel. Another diversity is that in some the hot vapour surrounds the extraction vessel and so heats the liquid during extraction, whilst in others the hot vapour passes up a side tube and so the liquid remains comparatively cool. A third diversity is that in some the floating solvent overflows back into the receiver, whilst in others it is siphoned back.

Apparatus of the Perpluviation Type.

Schwarz's apparatus (Fig. 27).—This appears to have been the first apparatus designed for the automatic extraction of liquids. The liquid is placed in the flask E, and the solvent, which must be lighter than the liquid, is placed in the receiving flask R, and is there boiled. The vapour ascends through the tube *t* to the upper vessel V, and thence through the tube *c* to a reflux condenser. The condensed solvent descends the tube *p*, then rises through the liquid in E, and collects as a layer above it until it reaches the opening into the side tube *q*, when it overflows and returns to the flask R. This circulation goes on automatically, and when on testing a drop of the overflowing solvent, the extraction is found to be complete, water is poured down V until all the solvent overflows down *q* into R; the parts are then disconnected, E is emptied, and by reconnecting and heating R, the solvent can be distilled off into E, leaving the desired substance in R. At *a* and *b* are mercury joints, which enable connection and disconnection to be readily made (Zeitsch. anal. Chem. 1884, 23, 368).

Yoder's apparatus (Fig. 28).—This is a simple form of apparatus which was used to extract certain organic acids from aqueous solutions by means of ether. The liquid is placed in the inner vessel E, which is supported at *d* by three dents in the outer tube. The vapour of the solvent passes up from the receiver through the hole *h*. If the solvent is lighter than the liquid the long funnel tube *f* is used. This is closed at the bottom, except for some small perforations in the end, which is slightly enlarged. The solvent from the condenser C passes down this tube, then escaping through the perforations, it ascends through the liquid, overflows, and runs back into the receiver. The perforations must be small enough to prevent too rapid a flow of solvent, even when there is rapid condensation, or else some of the liquid may be carried over. For heavy solvents, such as chloroform, the inner vessel is shaped like E′ and the funnel tube *f* is omitted, or else shortened so as only just to reach the surface of the liquid in E′, and is suspended from the top; the solvent passes downwards through the liquid, then up the narrow side tube, and overflows. When commencing, some of the solvent must be poured into E′ before pouring in the liquid, so that the side tube may contain solvent and not the liquid (J. Ind. Eng. Chem. 1911, 3, 641).

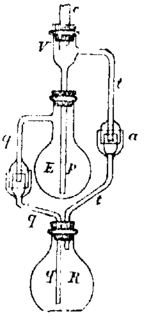

FIG. 27.

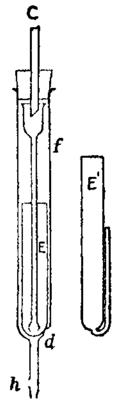

FIG. 28.

Van Rijn's apparatus resembles Yoder's, but the inner vessel has three constrictions, so that it takes the form of three bulbs and a cylindrical upper portion, and there are holes in the upper portion for the overflow of the solvent. At the lowest constriction there is a mark denoting the top of a definite volume in the lowest bulb (Ber. 1895, 28, 2387). Baum's apparatus for use with heavy solvents is like Yoder's, but the vessels are wider (Chem. Zeit. 1904, 28, 1172). Lenz's apparatus is much like Yoder's, but to avoid using a cork he closes the top of the wide outer tube loosely with a metal condenser, which partly rests on and partly enters into it, and which has a pointed end to condense the vapour and drop the solvent into the funnel. The bottom of the funnel tube is notched instead of being closed and perforated. For heavy solvents the tube E′ is covered with a cup-shaped piece of nickel wire gauze. By substituting for E a tube ending beneath in an open point it can be used as a percolation apparatus for solids (Arbeiten aus dem Pharm. Inst. Univ. Berlin, 1909, 7, 289).

Schacherl's apparatus (Fig. 29).—This is for use with light solvents, the liquid is placed in the extraction vessel E, filling it up to the bottom of the neck; if insufficient to do this, it can be diluted. The solvent is boiled in the receiver R, and the vapour passes up the tube *t* to the condenser at C; the condensed solvent drops into the funnel tube *f*, and when the column is sufficiently high, it passes up in drops through the liquid, collects in the neck of E, and overflows back into R. Corks can be avoided by using ground-in joints (Zeitsch. Nahr. Genussm. 1901, 4, 674).

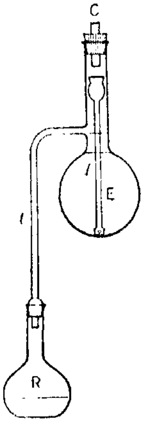

Fig. 29.

Fiske's apparatus (Fig. 30).—For large volumes of liquid Fiske has described an apparatus which, with the exception of the trap beneath the condenser, can be fitted up with ordinary pieces of apparatus. The ether or other light solvent is boiled in the distilling flask R, and the vapour ascends through a bulb C to a condenser. The tube *t* is sealed into this bulb, and rises a short way into it, so that the returning condensed solvent is trapped and led off by the tube *p* to the bottom of a common distilling flask E, containing the liquid, which should reach up to the bottom of the neck. The solvent passes up through the liquid, collects in the neck of E, and overflows through the tube *q* back into R. The liquid, when sufficiently extracted, is drawn off by the siphon *s*, and fresh liquid is introduced through the funnel tube *f*, which should end below the surface of the liquid, so that vapour cannot escape that way. In an experiment with this apparatus 540 c.c of an aqueous solution containing 6·4 p.c. of succinic acid yielded 67 p.c. of the acid to ether in 2½ hours (Amer. Chem. J. 1909, 41, 510).

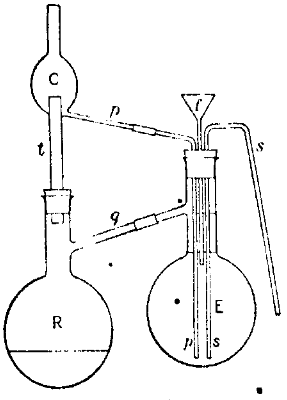

Fig. 30.

Bowman's apparatus (Chem. Soc. Proc. 1906, 22, 24) is somewhat on the same plan as Fiske's.

Friedrichs' apparatus (Fig. 31).—In order that the drops of a light solvent may traverse as long a path as possible as they rise to the surface of the liquid, Friedrichs makes use of a glass contrivance S, the surface of which is shaped like the thread of a screw. His condenser, only the bottom of which is shown in the figure, also employs a screw device. The vapour of the solvent passes from the receiver R up the side tube *t*, to the condenser C, and the liquefied solvent falls into the funnel tube *f*, and escapes by apertures at the bottom beneath the screw contrivance, and then follows a winding course along the thread till it collects above the liquid and is siphoned off by the tube *s*. The funnel tube *f* passes down the centre of S, into which no liquid enters. The siphon tube *s* runs outside the extraction vessel until it reaches *c*, where it passes into the bottom tube and returns the solvent to the receiver. The side funnel F and the tap T serve to introduce and remove liquid from the extraction vessel as required (J. Amer. Chem. Soc. 1912, 34, 285; and Zeitsch. angew. Chem. 1912, 25, 158). Friedrichs has also described a somewhat similar form, but with the receiving flask at the side, in Zeitsch. anal. Chem. 1911, 50, 756; and an apparatus for using liquefied gases as solvents for extraction at low temperatures in Zeitsch. angew. Chem. 1913, 26, Aufsatz. 201; and in J. Amer. Chem. Soc. 1913, 35, 244.

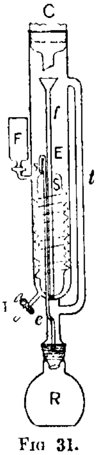

Fig 31.

Kempf's apparatus attains the same end as Friedrichs', namely, a long course for the drops of solvent rising through the liquid, by surrounding the funnel tube with a flat glass spiral winding upwards like turret stairs. This is placed in an extraction vessel, with holes near the top for overflow, and this, in turn, is placed in an outer vessel, as in Yoder's and van Rijn's forms (Chem. Zeit. 1910, 34, 1365). Kutscher and Steudel (Zeitsch. physiol. Chem. 1903, 39, 473) wind a glass spiral, apparently of thin rod, round the funnel tube. Kempf (Chem. Zeit. 1913, 37, 774) describes a form in which the liquid is kept cool by circulating water round it; in this, too, a spiral is used.

A third plan of increasing the path of the drops of solvent is to place the liquid in a spiral tube and make the solvent divided into small drops ascend through it, and then collect and return to the receiver. This is adopted by Partheil and Rose (Zeitsch. Nahr. Genussm. 1902, 5, 1049); by Jerusalem (Biochem. Zeitsch. 1908, 12, 379), who gives directions for extracting sap-like materials; and in Koolman's 2nd apparatus (*ibid.* 1911, 34, 481).

C. von der Heide's apparatus (Fig. 32).—In this a fourth way of increasing the duration of contact between the rising light solvent and the liquid is adopted, namely, by means of a series of inverted cups fused on to the funnel tube *f*, which fits into the extraction vessel E containing the liquid. The vapour from the solvent rises up the side tube *t*, and passes through the hole *h*, which corresponds to a similar hole *h'* in the funnel tube *f*; thence it passes to the condensing cup C, in which is placed a condensing spiral of twelve turns closely wound round a central cylinder (not shown in the figure). The liquefied solvent escapes from the notched end of *f*, and works its way from one cup to another through the small holes on alternate sides shown in them; as these are low down in the cups a little solvent is held in each cup. After collecting above the liquid the solvent overflows through *q* back to the receiver. Von der Heide also describes a still more complicated apparatus for either light or heavy solvents in which the cup device is employed, and further gives a third apparatus of the hot vapour injection type (Zeitsch. Nahr Genussm. 1909, 17, 315). Aron (Biochem. Zeitsch. 1913, 50, 386), like von der Heide, employs inverted cups.

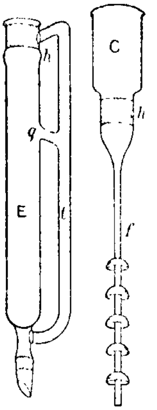

Fig. 32

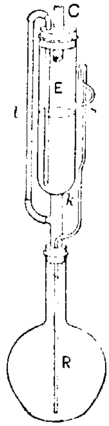

Fig. 33.

A fifth way of increasing the contact is to employ a current of air or other gas; this is used in Koolman's first apparatus (Biochem. Zeitsch. 1911, 34, 481), and by Berl (*see* below). Emde's method (Apoth. Zeit. Berlin, 1909, 24, 663) differs from all others by making the liquid pass through the solvent which is placed in a separator. The liquid enters in small drops from a jet just penetrating the upper surface of the solvent, collects at the bottom, and escapes through the tap and up a side tube; whence it can be made to pass similarly through other separators. Meeker (8th Int. Congress of Applied Chem 1912, 17, 45) describes a seventh and very original way, especially adapted to prevent emulsification. The solvent and liquid form two layers in a suitable vessel, in which there are two propellers on a vertical shaft, one in each layer. These propellers are so shaped as to thrust in opposite directions, the lower one thrusting upwards and the upper one downwards. It is claimed that at a suitable rate of rotation of the shaft fresh surfaces of liquid and solvent can be brought into contact without the formation of emulsions. A form with a revolving stirrer is described by Zelmanowitz (Biochem. Zeitsch. 1906, 1, 253) for extracting large volumes of aqueous liquid with light solvents, and a simplification of this is described by Tolmacz (Chem. Zeit. 1913, 37, 1381).

The following are references to other apparatuses for extracting liquids by perpluviation.

When the solvent is heavier than the liquid: Stephani and Böcker (Ber. 1902, 35, 2698), the solvent rains through the liquid, collects, and passes down to the receiver through a tube with a tap, which has to be adjusted so that just as much flows down as falls in from the condenser. A pad of glass wool can be inserted to break up emulsions. It can also be used for solids. Pregl's apparatus (Zeitsch. anal. Chem. 1901, 40, 785), that of Berlin (D. R. P. 251459, 1911), and that of Greenwald (J. Ind. Eng. Chem. 1915, 7, 621), are ingenious and compact.

When the solvent is lighter than the liquid: Neumann's 2nd apparatus (Ber. 1885, 18, 3061). Eiloart's 2nd apparatus (Chem. News, 1886, 53, 281), it resembles that in Fig. 34, except that the tubes are arranged so that the vapour goes to the condenser and the liquefied solvent passes down into E. Kurbatow (J. Russ. Phys. Chem. Soc. 1894, 26, [1] 39; and Ber. 1894, 27, 314R). Wroblewski's 1st apparatus (Zeitsch. anal. Chem. 1897, 36, 671). Foerster (Chem. Zeit. 1898, 22, 421) uses a tall cylindrical jar to hold the liquid; he gives particulars about extracting with ether soap solutions obtained from fats to get cholesterol and phytosterol. Kumagawa and Suto's apparatus (Beitr. Chem. Physiol. Pathol. 1903, 4, 185) is somewhat like Yoder's, but with much more glass-blower's work. Saiki (J. Biol. Chem. Baltimore, 1909, 7, 21) adapts an ordinary Soxhlet (Fig. 14) for liquids by slipping in a small bottle with a funnel tube standing in it. Bacon and Dunbar (J. Ind. Eng. Chem. 1911, 3, 930) use a flask having a very wide neck about 16 inches long, in which is hung a test tube containing the liquid and funnel tube, in this neck there is also contained the condenser hanging from an enlargement of its top, thus there are no corks or joints.

When the solvent is either heavier or lighter than the liquid: Wollny (Zeitsch. anal. Chem. 1885, 24, 54 and 202). Grauer (Dingl. poly. J. 1886, 262, 475) forms on a manufacturing scale. Diepolder (Ber. 1897, 30, 1797), Göckel (Zeitsch. angew. Chem. 1897, 683), and Hahn (Chem. Zeit. 1913, 37, 880) forms with movable interior vessels. Landsiedl (Chem. Zeit. 1902, 26, 274), several forms with movable interior vessels for use with solvents of high or low boiling-points.

Apparatus of the Injection Type.

Mameli's apparatus (Fig. 33).—In this apparatus the plan of forcing the hot vapour of the solvent through the liquid is adopted. It is somewhat like Soxhlet's apparatus, but the siphon *s* is attached at a point rather more than halfway up the side of the extraction vessel E, and reaches to the bottom of the receiver R to prevent the vapour escaping that way, also the tube *t*, which conducts the hot vapour from R bends over and reaches nearly to the bottom of E. Thus the hot vapour is forced through the liquid, and the condensed solvent collects above the surface of the liquid until the siphon is filled and put in action. There is a condenser at C, which liquefies escaping vapour and returns the solvent to E. A similar apparatus, but easier to fit up, employs instead of E a similar vessel having no siphon, but a long central tube passing down through a corked opening at *k*, and reaching from a point far up in E to the bottom of R, so that the floating solvent flows down it into R. The top of this tube can be bent over for a short distance if a siphoning action is desired. The side tube *t* passes through the cork of R, thus no glass-blower's work is required (Gazz. chim. ital. 1906, 36, 123).

Pelizza's apparatus is an injection form somewhat like Mameli's, but the floating solvent instead of being siphoned off, returns down a central tube, and the tube supplying the vapour bends down outside the extraction vessel and enters at the bottom; further, there is a close-fitting outer casing fused on to E, through which water circulates on its way to the condenser (Chem. Zeit. 1904, 28, 186). Moreschi and Simoni's apparatus resembles Mameli's, but the tube in the extraction vessel down which the vapour passes is surrounded by a condensing jacket through which cold water can be made to circulate (Rend. Soc. Chim. Ital. 1913, 5, 159).

Kiloart's 1st apparatus (Fig. 34).—In this the liquid is contained in the tall jar E. The vapour of a light solvent, which is boiled in the flask R, is forced through the liquid by means of the long tube *t*, *t*, which terminates in a small inverted funnel attached by fusion. The mouth of this funnel is covered with a piece of platinum foil perforated with holes. The top of the jar is tightly corked, and the solvent, which collects as a layer on the liquid, is forced up the tube *p* to the bottom part of a condenser C, and returns to R down the tube *q*. (It would be better if the cork at the bottom of C could be avoided by some glass contrivance.) The tube *t* is given considerable height to prevent any of the liquid in E being sucked back when R cools (Chem. News, 1886, 53, 281).

Neumann, in 1885, described his 1st apparatus in which ether vapour is forced into the liquid contained in a tall cylindrical jar and the floating ether is siphoned back into the receiving flask (Ber. 1885, 18, 3061).

Pip employs a vessel somewhat resembling an inverted gas jar, but having a small extra tubulure near the main tubulure. The liquid is contained in this jar, and the vapour of a light solvent from a receiving flask at the side is forced in at the bottom through a cork and tube fixed in the main tubulure, and is distributed through a perforated porcelain plate. A tube which passes through the small tubulure and reaches to a point above the surface of the liquid, leads the liquefied solvent back into the receiving flask. The tube supplying the vapour rises outside the jar and well above it and then bends down to reach the cork. There is a cork cover that supports a winding cooling tube in the liquid and a funnel (Chem. Zeit. 1903, 27, 706).

Wollny's apparatus (Fig. 35).—In this apparatus an idea is borrowed from the Bunsen burner, namely, to force a jet of vapour and a jet of condensed solvent up through a tube immersed in the liquid, thus attaining a close intermixture. The apparatus is connected by mercury joints: below to a receiving vessel, and above to a condenser. The vapour of the solvent, which can be introduced if so desired by the side tube *p* instead of from the receiving vessel, passes up the tube *t*, which rises nearly to the top of the apparatus, bends down forming an inverted U, enters the extraction vessel E at the bottom, and terminates in a jet. A funnel tube *f* conducts the liquefied solvent from the condenser and delivers it by a jet alongside the vapour jet in the mixing tube *m*, in which an intimate mixture of liquid and solvent is made and overflows at the top. The tube *m* is surrounded at the top by a wider tube *w*. When the solvent is heavier than the liquid the tube *q* is employed, and is placed over the exit tube *s*, which reaches down nearly to the bottom of the receiving vessel; the pressure of the liquid then supports a column of solvent, indicated in the figure by the shading, as high as the top of *s*, and the solvent flows off down *s*. The liquid is not shown in the figure. There is no siphoning action as *q* is open at the top. When the solvent is lighter than the liquid the tube *q* is removed; the solvent now floats on the surface of the liquid and runs off down the tube *s*. The loose parts are suspended from the upper edge by platinum wire. Wollny states that the apparatus is suitable when the solvent and liquid separate quickly after intermixture, and that an emulsion is not so likely to form at boiling temperature as when the liquid and solvent are cold. [Other authors state, however, that warmth promotes emulsification.] In case of an emulsion forming, he suggests leading aside the condensed solvent out of the apparatus for a time and allowing vapour only to pass in as a means of effecting separation. He also describes several other somewhat similar forms of apparatus (Zeitsch. anal. Chem. 1885, 24, 47 and 202).

Berl's apparatus is on the same plan as Wollny's, but is even more complicated. In it the vapour of a light solvent and a current of air or some other gas are forced up a glass spiral

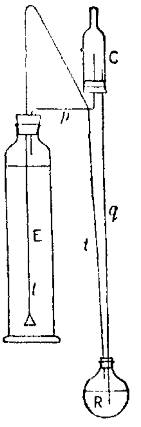

FIG. 34.

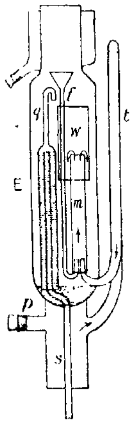

FIG. 35.

immersed in the liquid, so that some of the liquid accompanies them, the mixture is discharged at the top of the spiral and falling back rejoins the main body of the liquid (Chem. Zeit. 1910, 34, 429).

The following are references to other injection forms: Hagemann (Ber. 1893, 26, 1975), for heavy or light solvents. Wroblewski's 2nd apparatus (Zeitsch. anal. Chem. 1897, 36, 672), for light solvents, the tube that conveys the overflowing solvent back to the receiver dips to form a U-tube and rises again to enter the receiver. There is a tap at the bottom of the U-tube, so that any drops of the liquid that come over can be removed before reaching the receiver, and also portions of the solvent can be taken for testing. Lentz (Chem. Zeit. 1901, 25, 820), for chloroform, it can be easily fitted up with ordinary apparatus. Fritsch (Chem. Zeit. 1909, 33, 759), for use with ether, the liquid is contained in an inverted Woulfe's bottle, or by putting calcium chloride solution instead of the liquid it can be used to purify ether. C. von der Heide (Zeitsch. Nahr. Genussm. 1909, 17, 315). Tcherniac (Chem. Soc. Trans. 1919, 115, 1090), an elaborate apparatus for forcing ether vapour from one flask into an aqueous liquid contained in another, which is immersed in water so that it can be kept cold or allowed to get warm as desired. A device is employed by which any aqueous liquid carried away by the ether is returned to the extraction flask and does not reach the receiving flask. When in good order it can be left to work overnight. H. H. R.

F

F-ACID. 2-Naphthylamine-7-sulphonic acid *v.* NAPHTHALENE.

FACTIS (*Faktis, Factice, Parafactis*). A general term applied to so-called rubber substitutes prepared from oils.

White substitute is made by stirring sulphur monochloride into linseed, rape-seed, refined colza oil, or other unsaturated oil with or without admixture of petroleum spirit. A considerable rise of temperature occurs, the oil thickens, and, when the reaction has proceeded far enough, the whole is poured into trays, and solidifies to an elastic solid, somewhat resembling rubber. It is necessary to control the temperature, and therefore only limited charges of material are used.

The product is an additive compound of the oil and sulphur monochloride, and consists mainly of the glycerides of fatty acids containing chlorine and sulphur (Ulzer and Horn, Jahresb. Chem. Technol 1890, 1177; Henriques, Chem. Zeit. 1893, 707).

Dark or **French substitute** is obtained by heating a vegetable oil to 200°, and stirring in sulphur. The liquid thickens, and on cooling solidifies to a black elastic solid. It is sometimes prepared from rape-seed oil or cotton-seed oil which has previously been partially oxidised by treatment with air at a high temperature (*v., e.g.*, Eng. Pat. 15163, 1899). Substitutes manufactured from these 'blown oils' have a sp.gr. less than 1, and are accordingly known as 'floating substitutes' (*v.* Altschul. Zeitsch. angew. Chem. 1895, 535).

A wet method of manufacture consists in oxidising the oil with dilute nitric acid at 100°, and then adding colophony, spirit of turpentine, sodium chloride, and sodium polysulphide, and boiling till the factis has the proper consistency. It is then finally washed, dried, and rolled (*v.* Lutenaf. Rev. Prod. Chim. 3, 147; J. Soc. Chem. Ind. 1900, 673).

These preparations, however, have only a limited application as rubber substitutes because of their small elasticity and insolubility in the usual rubber solvents. Also they are easily hydrolysed by steam and other agents. If excess of oil and sulphur are first removed from the factis by treatment with carbon disulphide, acetone, &c., they may be incorporated with a proportion of pure rubber, and their usefulness much increased (Ditmar, Fr. Pat. 377538, 1907; J. Soc. Chem. Ind. 1907, 1058; *v. also* Cherchoffsky, D. R. P. 218225, 1908; J. Soc. Chem. Ind. 1910, 440; and Heil and Esch, Manufacture of Rubber Goods, 110).

FAHLORE. A partial translation of the old German name *Fahlerz*, applied, like the term 'grey-copper-ore,' to minerals of the tetrahedrite group. These are essentially sulphantimonites or sulpharsenites of copper with the general formula $R'_3R'''S_3$, where R′ represents copper and silver, and R‴ antimony, arsenic, or, exceptionally, bismuth. In many instances, however, small amounts of iron and zinc (less often mercury, lead, or cobalt) are also present, and the formula then becomes

$$R'_3R'''S_3+n(6R''S\cdot R'''_2S_3)$$

where R″ represents iron, &c., and n is a small fraction usually $\frac{1}{10}$ or $\frac{1}{4}$ (Prior and Spencer, Min. Mag. 1899, xii. 202). A. Kretschmer (Zeits. Kryst. Min. 1910, xlviii. 484) gives several new analyses and writes the formula in the form $(R'_x, R''_y)_3R'''S_{3+\frac{y}{2}}$. Owing to this wide range of isomorphous replacement, the actual composition of fahlore is extremely variable, as is illustrated by the following analyses. Further, owing to the fact that fahlore usually forms intimate intergrowths with other minerals, more particularly copper-pyrites it is probable that many of the older analyses were made on material which was not ideally pure.

—	I	II	III	IV	V	VI
S	24·48	24·33	23·15	27·60	21·17	22·96
Sb	28·85	28·32	27·73	—	24·63	21·35
As	trace	trace	trace	19·04	—	—
Bi	...	0·83	—	—	—	—
Cu	45·39	41·55	30·56	49·83	14·81	34·57
Ag	—	—	15·26	1·87	31·29	—
Fe	1·32	1·02	3·51	1·11	5·98	2·24
Zn	—	2·63	trace	—	0·99	1·34
Hg	—	—	—	—	—	15·57
Pb	0·11	0·62	0·05	0·17	—	—
	100·15	99·30	100·26	99·62	98·87	98·03
Sp.gr.	4·921	4·969	5·047	4·62	—	5·107

I, Tetrahedrite from Fresney d'Oisans, Isère, France (G. T. Prior, 1899); II, tetrahedrite from Horhausen, Rhenish Prussia (G. T. Prior, 1899); III, tetrahedrite from Wolfach, Baden (G. T. Prior, 1899); IV, tennantite ('binnite') from Binnenthal, Switzerland (G. T. Prior, 1899); V, argentiferous tetrahedrite (freibergite) from Freiberg, Saxony (H. Rose, 1829); VI, mercurial tetrahedrite (schwartzite) from Schwarz, Tyrol (Weidenbusch, 1849).

Many of the names which have been applied to the minerals of this group express these differences in composition. Tetrahedrite (Fr. *Panabase*) and tennantite denote the antimonial and arsenical series respectively, and these are usually regarded as species; other names take the rank of varieties under these. For example, freibergite (Ger. *Weissgültigerz*) is a variety of tetrahedrite containing much silver: schwartzite is a mercurial tetrahedrite; and malinowskite one containing lead. In the arsenical series, or tennantite, the names sandbergerite and kupferblende are applied to varieties rich in zinc; rionite and annivite to those containing bismuth.

Although differing so widely in chemical composition, all varieties of fahlore are identical crystallographically, the type of symmetry being that of the tetrahedral class of the cubic system. A pronounced tetrahedral habit of the crystals is extremely characteristic of the antimonial members (hence the name tetrahedrite), whilst in the arsenical series (tennantite) this is often somewhat masked by the greater development of the rhombic dodecahedron. The colour is iron-black to steel grey, and the lustre metallic and often brilliant. The fracture of pure material is typically conchoidal, with a brilliant lustre. The streak is usually black, but in some specimens (those containing but little iron) it is dark reddish-brown; hardness, 4; sp.gr. 4·4–5·1.

Fahlore occurs in mineral-veins in association with other metallic minerals. Beautifully crystallised specimens have been found in many mining districts, notably at the Herodsfoot Mine near Liskeard in Cornwall, Clausthal in the Harz Mountains, Kapnik in Hungary, &c. In the massive condition it is, at times, found in some abundance, *e.g.* in Nevada and Utah, and it is then an important ore of copper. The bulk of the rich silver ores of Bolivia and Peru consist of argentiferous tetrahedrite.

L. J. S.

FARINA, or POTATO STARCH. The starch of the potato, *Solanum tuberosum* (Linn.). The tubers are placed in a cylinder furnished with teeth by means of which the starch cells are lacerated whilst the mass of potatoes is reduced to a stiff pulp. The starch granules are washed out and allowed to settle in vessels of water, when the water is drawn off. The moist starch, after being separated from the cellulose, is dried and broken up between iron rollers. It is then ready for its purpose, which is in the main the sizing of textiles.

As a material for the purpose of sizing, farina produces when boiled a thicker paste than any other starch; consequently, a small amount of it will furnish a liquor of the same density as a much larger quantity of, for instance, wheaten flour. On the other hand, the starch cells of the potato being exceptionally large, a certain amount of coarseness is felt in cotton goods stiffened by it. For this reason, it is seldom used with China clay alone, but is usually mixed with a greater or smaller proportion of flour. It is claimed for farina that, since the potato contains a small amount of nitrogenous matter, it is not so prone to induce mildew in cotton goods as are other forms of starch.

Farina has a glistening appearance and a crisp feeling when pressed between the fingers. It contains a larger proportion of moisture than any other starch, varying from 17 to 20 p.c. The granules are very characteristic, being for the most part large, though irregular in size, and resembling an oyster-shell in form, being, moreover, marked with similar eccentric rings.

The following is the average composition of ordinary commercial farina:—

Water	16·72
Cellulose	0·36
Ash	0·22
Starch	82·70
	100·00

Farina is preferred to other starches for the manufacture of British gum, its great purity making it especially suitable for this purpose (*v.* Starch).

FARNESOL, an alcohol found by Haarmann and Reimer in the oil of quassia flowers. It is found also in Peru and tolu balsam and palmarosa oil, and also, by Elze (Chem. Zeit. 1910, 34, 857), in cananga oil from Java. It is optically inactive; sp.gr. 0·985 at 15°, and boils at 145°–146° at 3 mm.

FAST ACID FUCHSIN, -SCARLET *v.* Azo-colouring matters.

FAST-BLACK, -GREEN M *v.* Oxazine colouring matters.

FAST BLUES *v.* Indulines.

FAST BORDEAUX *v.* Azo-colouring matters.

FAST BROWN N, ACID BROWN, NAPHTHYLAMINE BROWN *v.* Azo-colouring matters.

FAST COTTON BLUE, -BROWN *v.* Azo-colouring matters.

FAST PONCEAU B and **2B, BIEBRICH SCARLET, PONCEAU 3R** or **3R B,** *v.* Azo-colouring matters.

FAST REDS or **ROCELLIN, RUBIDINE, ORSEILLINE** *v.* Azo-colouring matters.

FAST SCARLET *v.* Azo-colouring matters.

FAST SULPHONE VIOLETS *v.* Azo-colouring matters.

FAST YELLOW *v.* Azo-colouring matters.

FAT LUTE *v.* Lutes.

FATTY ACIDS. A numerous and important group of acids of the general formula $C_nH_{2n}O_2$, certain members of which are essential constituents of the animal and vegetable fats. The lowest term of the series is formic acid H·COOH; the highest term at present known is dicetylic acid $C_{34}H_{68}O_2$. As the radical C_nH_{2n+1} may exist in a variety of modifications, it follows that the fatty acids are also capable of existing in numerous isomeric forms. The fatty acids may, like the monovalent alcohols, be distinguished as primary, secondary, and tertiary. The secondary acids are usually termed *iso-acids,* whilst the acids containing the groups $CH_3 \cdot CH_2 \cdot CH_2 \cdot \ldots$ are called *normal acids.*

The naturally occurring fatty-acids are found partly free and partly in the form of esters. Formic acid is found in ants, caterpillars, and in the stinging-nettle; butyric acid in butter, in perspiration, and, combined with hexyl alcohol, in the fruit of *Heracleum villosum* (Fisch.); cerotic acid in bees-wax; stearic acid in animal fats, &c. The higher members of the series, in combination with glycerol, forming the so-called *glycerides,* constitute the greater part of the more important animal and vegetable fats and oils and the different varieties of the waxes.

The lower members of the series, formic, acetic, propionic, acids, &c., are mobile volatile liquids, miscible with water, alcohol, and ether in all proportions. As the number of carbon atoms increases, they become less soluble in water, more oily and viscid, and less volatile. Thus œnanthylic (*heptoic*) acid $C_7H_{14}O_2$ is insoluble in water; capric (*decylic*) acid $C_{10}H_{20}O_2$ is solid at ordinary temperatures; whilst lauric acid $C_{12}H_{24}O_2$ and the higher homologues cannot be distilled under ordinary pressure without decomposition.

The most important general methods of obtaining these acids are:

(1) By the oxidation of the primary alcohols or aldehydes, *e.g.* ethyl alcohol → acetic acid.

(2) By the addition of hydrogen to the unsaturated monocarboxylic acids, *e.g.* acrylic acid → propionic acid.

(3) By the reduction at high temperatures of hydroxy-acids with hydriodic acid or of halogen substituted acids with sodium amalgam, *e.g.* α-hydroxypropionic acid → propionic acid.

(4) By heating the acid nitriles with acid or alkali, *e.g.* acetonitrile → acetic acid.

(5) By decomposing ketones through oxidation with potassium permanganate, *e.g.* pentadecylmethylketone (obtained from palmitic acid) → pentadecylic and acetic acids.

(6) By decomposing unsaturated acids by fusion with caustic potash, *e.g.* oleic acid → palmitic and acetic acids.

(7) By decomposing the mono- and dialkylacetoacetic esters with concentrated potash solution, *e.g.* diheptylacetoacetic ester → diheptylacetic acid.

(8) By heating dicarboxylic acids, in which the two carboxyl groups are in union with the same carbon atom; *e.g.* dicetylmalonic acid → dicetylic acid.

The more important transformations which the fatty acids can be made to undergo are as follows:—

(1) Acids and alcohols yield *esters* in the presence of hydrochloric or sulphuric acids.

(2) The halogens react, producing substitution products.

(3) Acids or their salts, when acted on by the chlorides of phosphorus, yield *acid chlorides* and *acid anhydrides.*

(4) The ammonium salts of the acids split off water and become *acid amides* and *acid nitriles.*

(5) *Primary amines* are produced by the reduction of the acid nitriles and by the action of bromine and sodium hydroxide on the acid amides. In the latter case, carbon dioxide is evolved and the primary amine of the next lower acid is produced.

(6) When the calcium salts are distilled with calcium formate, *aldehydes* are produced, but, when distilled alone, the calcium salts yield *ketones.*

(7) *Paraffins* are produced by the reduction of the higher fatty acids with hydriodic acid, by the electrolysis of concentrated solutions of the potassium salts of the acids and by the distillation of the calcium salts with soda lime.

The various members of the fatty acid series are described under their separate headings.

FAVERSHAM POWDER *v.* EXPLOSIVES.

FAVIER'S EXPLOSIVE *v.* EXPLOSIVES.

FAYALITE *v.* OLIVINE.

FAYENCE *v.* POTTERY and PORCELAIN.

FEATHER-ALUM. A name (Ger. *Federalaun*) applied by Klaproth in 1802 to the iron-alum ($FeSO_4 \cdot Al_2(SO_4)_3,24H_2O$) now known as halotrichite (*q.v.*). Like alunogen (*q.v.*), kalinite (potash-alum), pickeringite (magnesia-alum), &c., it occurs as a delicately fibrous efflorescence on shale and some other rocks; and it is possible that these species also may have at one time or another been included under the indefinite term 'feather-alum.' L. J. S.

FEATHER-ORE. A popular term (Ger. *Federerz*) applied to a number of finely fibrous minerals, which possess in common a lead-grey colour with metallic lustre. The material forms delicate tufts or felt-like masses. Brittle 'feather-ore' is referable to jamesonite (*q.v.*), since this possesses a good cleavage perpendicular to the length of the fibres. On the other hand, flexible 'feather-ore' may be stibnite (Sb_2S_3), plumosite ($2PbS \cdot Sb_2S_3$), or one of the several other fibrous sulphantimonites of lead (Spencer, Min. Mag. 1907, 14, 207). L. J. S.

FECULOSE is the term by which the various commercial starch esters are designated. They are best formed by the action of glacial acetic acid on starch, and then washing the product with cold water to free it from uncombined acid. By varying the starch base and the time and temperature of the reaction, or the concentration of the acid, an endless variety of products may be obtained according to the purpose for which they are required.

Feculose differs little in appearance or in ordinary chemical properties from ordinary starch. On boiling with water, it gives a clear homogeneous solution which does not set or revert on standing, gives the usual blue colour with iodine, and does not reduce Barreswil's (Fehling's) solution. When a little of the solution is allowed to dry on a clean glass plate, it forms a clear flexible film equal to that of the finest gelatin. The washed feculose is neutral or slightly acid, and reacts with most chemical reagents more readily than ordinary starch.

Uses.—Feculose has been described as an ideal substitute for gelatin and vegetable gums. It has been applied as a special textile finish to confer lustre and substance to textiles in the form of yarn or cloth and also as an excellent dressing for linen, lace, and silk. It is also employed in dyeing and French cleaning; in confectionery for making jujubes and other sweets, and in paper coating as a size in place of 'chromo' glue or casein. The surface produced in the latter case has excellent printing qualities.

A permanent solution of feculose can be obtained by varying the original process of manufacture, and by various subsidiary treatments it can be made to fulfil a large range of technical requirements (Traquair, J. Soc. Chem. Ind. 1909, 288; Farrell, J. Soc. Dyers, Dec. 1908).

FEEDING STUFFS. Under this head will be considered the principal articles in use as food for live stock

The main constituents of feeding stuffs, apart from water, are (1) nitrogenous bodies, subdivided into albuminoid or proteid substances and non-albuminoid bodies, such as amides; (2) oil or fat; (3) carbohydrates, including easily digestible substances like sugar or starch, and indigestible or less easily digestible bodies of the cellulose type; (4) the so-called 'mineral' constituents which constitute the 'ash' left on incineration. There are also frequently present other bodies, such as resinous matters, colouring matters, enzymes, and traces of glucosides and organic bases of the alkaloidal type; but these exist in relatively small quantities, and are usually ignored in commercial analyses. Small quantities of neutral or acid organic salts are also found in roots and green fodder crops.

Albuminoids or Proteins. These are bodies consisting of highly complex molecules built up by the union of numerous amino-acids (*see* article on PROTEINS, vol iv.). The various proportions in which these amino-acids are combined, and the presence or absence of some one or other of them in the complex molecule, results in there being a large variety of proteins or albuminoids: so that the proteins in one food may possess different properties from those in another food. The albuminoids of wheat, for example, have properties which sharply distinguish them from those of other cereals, such as barley, oats, or maize, and the albuminoids of the leguminous grains differ from those found in any of these. The detailed study of the albuminoids has engaged much attention at the hands of physiological chemists, and is gradually throwing light on much that has been obscure as to the relative feeding value for different purposes of albuminoids derived from different sources. Practical experience shows that a mixed diet is often productive of better results than a simpler diet which may supply the same aggregate quantity of nitrogenous matter. Of the various amino-acids constituting the albuminoid molecules, some few, such as tryptophane, cystine, arginine, and histidine, even though present in relatively small proportions, appear to be essential to satisfactory nutrition, and an albuminoid material lacking in one of these essentials consequently needs to be supplemented by another in which the missing factor is present. For example, the albuminoids of maize appear to be destitute of, or poor in, tryptophane. This affords an explanation of the fact that maize, while a satisfactory food for stock in conjunction with other foods, is unsatisfactory when given alone, its albuminoids, owing to the lack of tryptophane, being but imperfectly assimilated. The addition, however, of a small quantity of other food containing albuminoids of which tryptophane happens to be a constituent, renders the maize protein assimilable, and enables the animal to obtain the full advantage of the feeding matter contained in the maize. Albuminoids consist of carbon, hydrogen, oxygen, nitrogen, and a small quantity of sulphur. On the average, they contain 16 p.c. of nitrogen, and are usually calculated from the nitrogen present on this assumption. In some foods (*see infra*) the proportion of non-albuminoid nitrogenous compounds is sufficient to make it desirable to separate these in analysis, and to calculate the albuminoids from the true proteid nitrogen only. But in most concentrated foods it is conventional and sufficiently near for practical purposes, to calculate the albuminoids by multiplying the total nitrogen present by 6·25.

The chief function of albuminoids in food is to build up the nitrogenous tissue of the growing animal, and to replace the daily nitrogenous waste due to the normal processes of metabolism. Hence they have long been called 'flesh-formers,' in contradistinction to fat and carbohydrates. Albuminoids, however, are also capable of being partially transformed into fat, and also of generating heat and motive energy by their oxidation. These functions, however, are mainly performed by fat and carbohydrates.

The digestion of albuminoids is effected mainly by the action of pepsin, secreted by the stomach and of trypsin, which is a constituent of the pancreatic juice. By these ferments, they are converted into soluble bodies, peptones and albumoses, and finally broken down into their constituent amino-acids, which are then absorbed into the animal system, forming the materials for the reconstruction of the various proteins or albuminoids of the body, or used directly for the production of energy.

The non-albuminoid nitrogenous constituents of food, chiefly amides, are soluble and need no digestion. They do not form muscular tissue, like the albuminoids, but they yield heat and energy, and to some extent help to preserve the nitrogenous constituents of the body itself from waste.

Oil or Fat. A large number of fats are found in vegetable tissue. For the main part they are triglycerides of one or other of the series of bodies known as the 'fatty acids'; but they also include in some cases small quantities of wax or fat in which the glyceryl radical is replaced by that of some solid alcohol like phytosterol. Lecithin, which is present in small quantities in some vegetable substances, is a fat containing nitrogen and phosphorus. In the analysis of feeding stuffs, the matter extractable by ether is usually assumed to be fat, though in the case of some foods small quantities of resinous bodies are included in the extract, as well as chlorophyll.

The function of fat as a food is to build up the fat of the body and to furnish heat and energy on its oxidation or combustion in the blood.

Fat is digested and rendered absorbable into the blood mainly by the action of bile, aided by the pancreatic secretions and those of various intestinal glands.

Carbohydrates. Sugars of various types occur in feeding stuffs, sometimes in insignificant quantity, as in ordinary grain, sometimes in large quantity, as in some roots, the feeding value of which lies principally in these constituents. Thus mangolds and beets contain sucrose or cane sugar, whilst turnips contain dextrose or 'grape sugar.' In addition to sugars of the hexose type, some fodder plants yield sugars of the pentose type. Sugars, being soluble, need no 'digestion.'

Starch, which is practically perhaps the most important of the carbohydrates, consists of organised cells which are insoluble in cold water though capable of being gelatinised and partially dissolved by boiling water. Starch is convertible by mineral acids into sugar (dextrose), and is resolved by certain ferments, both vegetable and animal, into the soluble bodies maltose (malt sugar), and dextrin, a viscous body devoid of sweetness. The latter resolution is effected by the ferment *ptyalin* in the saliva, and also by a ferment contained in the pancreatic juice. The acid secretions of the stomach also act on starch, and the maltose and dextrin are further modified into dextrose during passage through the intestines.

Cellulose. Numerous substances are grouped under this head. The typical form of cellulose is cotton. Material of this nature forms the coating of vegetable cells, and consequently the whole 'skeleton' of a plant. But it is modified in composition in different tissues, and sometimes partially assumes a woody form, as in straw and hay. In food analyses, the various forms of cellulose are called 'fibre,' and are determined by boiling the food successively in weak mineral acid and weak alkali, and extracting with alcohol and ether. The residue is usually described as 'fibre' or 'crude fibre,' or sometimes as 'indigestible fibre.' The last description was given on the assumption that the artificial digestion referred to was equivalent in ultimate effect to the digestive processes of the animal. But modern research has shown that bodies of the cellulose type which resist the solvent treatments referred to are to a variable extent partially digestible, especially by ruminants. This digestion is probably mainly effected by the action of bacteria in the large intestine. A ruminant can digest much more cellulose than a horse, and a horse much more than a pig. The very thorough mastication of the ruminant better prepares the fibre for such digestion as is possible than does the imperfect mastication of the horse or the still more imperfect mastication of the pig, apart from the anatomical differences in the digestive tracts of the respective animals and the relative abundance of bacteria capable of effecting cellulose digestion. How much the physical or mechanical condition of the fibre has to do with its digestion has been demonstrated by Kellner, who found that, when straw fibre was disintegrated by boiling with soda lye under pressure (as in the preparation of fibre for paper making), the fibre had a digestibility coefficient of 56 to 60 p.c., whereas, in the unprepared straw, it was only 42 p.c. But the energy spent by the animal in the partial digestion of some forms of fibrous foods sometimes exceeds the energy-producing value of the material digested, so that the result of the digestion process may sometimes be of even negative value.

Other insoluble carbohydrates are those of the pentosan type, which yield pentose sugars on treatment with acids, but the conditions affecting their digestion are not well understood, and the feeding value of the pentoses which they yield is probably small.

The function of carbohydrates is to supply the main quantity of fuel for the generation of heat and the production of mechanical force, and, when these necessary requirements are fulfilled, the excess serves to build up fat in the body.

Mineral matters, or 'ash constituents,' are the residues left on incineration of the heterogeneous mass of organic compounds and salts contained in the food. Probably most of the 'mineral' matter thus obtained exists in the food in organic combination. The chief constituents of the ash are phosphoric acid, sulphuric acid, calcium, potassium, and magnesium, with smaller quantities of iron, sodium, and chlorine, and traces of fluorine. Silica is also a large constituent of straw, and is found in grass. Other elements are no doubt commonly present in minute traces.

The function of 'mineral' matters in food is to build up the main substance of the animal skeleton and to provide the material necessary for forming the saline constituents and inorganic acids of the blood, gastric juice, and other fluids and secretions of the body, as well as to supply elements, such as phosphorus, sulphur and iron, which form integral parts of the blood corpuscles and of muscular and other tissues.

The general composition of some of the various feeding stuffs in common use is stated in the accompanying tables. The items given are moisture (*i.e.* loss on drying at 100°C.), oil (ether extract), albuminoids, digestible carbohydrates, fibre and mineral matter (ash). The term 'digestible' as applied to carbohydrates here merely means rendered soluble during the process of successive boiling in weak mineral acid and weak alkali (for details see *Methods of analysis*, *infra*). The question of actual digestibility by the animal will be considered further on. The term 'albuminoids,' except where otherwise specified, means total nitrogen multiplied by 6·25, as is conventional for the purpose of commercial analysis. It has been already pointed out that the whole of the nitrogen in foods is not present in the proteid form, some portion being in the form of amides or similar bodies, but that in what are generally called 'concentrated' foods, such as seeds and seed products, the proportion of non-albuminoid nitrogen is relatively small, and not worth differentiation for the ordinary practical purposes of comparison of one sample with another. For instance, in barley, oats, maize, wheat, and rye, the actual albuminoid nitrogen is from 90 to 96 p.c. of the total nitrogen; in cotton cake, linseed cake, and ground-nut cake, and in brewers' grains, about 96 p.c.; in peas and beans, about 90 p.c.; in rice meal (rice bran), about 92 p.c.; and in wheat bran, about 86 p.c. In straw (a ripened stem, it may be noted), the proportion is about 90 p.c. In meadow hay it is less, namely, about 87 p.c. In young or immature grass or clover, the proportion is only from about 70 to 75 p.c., and in grass or clover preserved in the moist state as silage it may be only 50 to 60 p.c., owing to partial degradation of the albuminoids by fermentation. In roots, the proportion of albuminoid to total nitrogen may fall below 40 p.c. (as in mangolds). In turnips, carrots, and potatoes, it is from about 50 to 60 p.c., and in cabbages probably about 70 p.c.

Before referring to the tabulated statement of composition of various foods, the reader should bear in mind that the analyses given are in most cases typical only of the average composition of each, and that considerable differences occur between different samples, which is, indeed, the reason why many of them are ordinarily subjected to analysis for the purposes of commercial transactions. These variations are often considerable even in natural grains such as oats, but are especially notable in the case of what may be called 'manufactured' feeding stuffs such as oil cakes. The feeding value of these is largely affected by the extent to which the oil has been pressed from the seed. Thus linseed cake, if lightly pressed, may contain 15 or 16 p.c of oil. Under medium pressure, it may contain 12 p.c., and would still be regarded as rich in oil. Very commonly it is pressed down to 10 p.c., while very heavily pressed cake has often only 7 or 8 p.c. of oil, and sometimes, though rarely, as little as 5 or 6 p.c. Sometimes (or often in the case of cotton cake) the cake is ground and sold as meal. In such cases, it is especially important to have regard to the oil, as oil is largely extracted from some seeds, not by pressure, but by exhausting the finely ground seed with a volatile solvent such as petroleum spirit, in which case it may have only 1 p.c. of oil. This process is largely applied to rape seed, soya beans and palm-kernels. Again, in the case of linseed or rape cake, the percentage of albuminoids varies largely with the variety of seed from which the cake is made. Linseed cake, made from East Indian linseed, may contain from about 25 to about 30 p.c. of albuminoids; cake from Russian linseed, about 27 to about 35 p.c.; whilst cake made from American Western linseed sometimes contains nearly 40 p.c. of albuminoids. The composition of undecorticated cotton-seed cake varies according to whether it is made from the large smooth Egyptian seed or from the small thick-shelled and cotton-coated Indian variety. In the case of decorticated cotton-seed cake—made from American woolly seed stripped of its husk or 'hull'—the quality of the cake or meal depends largely upon the perfection with which the shelling process has been carried out. Often the separated shells are ground and partially put back after the decorticated seed has been crushed in the mills and the cakes reground to meal. Some foods are residual portions of grains, the main part of which is used for human food—as, for example, wheat-bran, rice meal (really rice-bran), and numerous foods made from various fractions of the maize kernel. These are necessarily of variable composition, according to the method and degree of separation from the other parts of the grain.

Owing to the importance of albuminoids in feeding, and to their special value for milch cows, and for balancing the natural poverty in albuminoids of natural fodders such as roots, 'concentrated' food stuffs are sometimes graded according to their richness in albuminoids. Thus decorticated cotton cake or meal, ground-nut (*Arachis*) cake, and soya-bean cake or meal, may be described as very rich in albuminoids (40 to 50 p.c.); linseed cake and rape cake as rich (say 25 to 35 p.c.); undecorticated cotton cake, beans, peas, and dried brewers' grains as moderately rich (20 to 25 p.c.); whilst wheat, oats, rye, barley, maize, feeding flour, rice meal, bran, pollards, and millet, would be described as relatively poor in albuminoids (10 to 18 p.c.).

In the case of fodder crops, such as grass and hay, the composition varies much with the stage of growth at which they are cut, as well as with the species of plants which constitute them.

The relative manurial value of the excreta yielded by the consumption of feeding stuffs depends largely on the proportion of nitrogen they contain, and to a minor extent on the phosphoric acid and potash contained in their ash. This aspect of their value is too complex to be entered upon here. A very full discussion of this part of the subject by Voelcker and Hall in the light of modern investigation, especially with regard to the question of compensation for unexhausted manurial value under the Agricultural Holdings Act, will be found in the Journal of the Royal Agricultural Society for 1902 and 1913.

Digestibility of feeding stuffs. It never happens in practice that an animal digests the whole even of the potentially digestible matters in its food. The quantity digested depends not only on the inherent potential digestibility of the food, but also on the species, age, condition, and individual constitution of the animal, and the quantity and quality of the food supplied to it. A large number of experiments have, however, been carried out, chiefly in Germany and in America, to ascertain as nearly as is practicable the proportion of the various kinds of nutritive matter actually digested in most of the feeding stuffs in use on the farm, the experiments having been made with the various farm animals, ruminant and non-ruminant. The composition of the food supplied to the animal is ascertained by analysis and its quantity weighed. The fæces are collected, weighed, and analysed, and the difference gives the quantity of each constituent digested. The experiments are carried on for a sufficient length of time to eliminate as far as possible errors due to previous feeding, the results for the first few days being neglected. The results, especially in the case of poor and bulky foods, are vitiated to some extent by such of the secretions of the alimentary canal as are voided with the excreta; while the results obtained with concentrated foods are complicated, and probably vitiated by the fact that such foods, in the case of ruminants, must necessarily be mixed with large quantities of bulky fibrous fodder, any variations in the digestion of which, brought about by the different conditions of feeding, become credited to the account of the concentrated food, which cannot be tried by itself. Despite these and other sources of inexactness, the study of the results of a number of experiments gives the nearest approach we can get to a faithful estimate of what proportions of albuminoids or of fat or of carbohydrates will *probably* be digested and utilised in the average circumstances of farm feeding, and much credit is due to such investigators as Kuhn, Wolff, Kellner, Zuntz, Armsby, and others for their long and patient labours in this field of work, in which the pursuit

Average or Typical Composition of Some Concentrated Feeding Stuffs.

—	Moisture	Oil or fat	Albuminoids (=total nitrogen ×6 25)	Digestible carbohydrates[1]	Fibre	Mineral matter (ash)	Sand or silicious matter in ash
Cotton cake, decorticated	9·0	11·5	44·0	23·0	5·5	7·0	—
Do., do., undecorticated, from Egyptian seed	13·5	6·5	22·5	33·0	19·0	5·5	0·4
Do., do., from Bombay seed	12·0	4·5	19·0	35·5	22·0	7·0	1·5
Soya-bean cake	12·5	7·0	42·0	28·5	4·5	5·5	0·5
Earth-nut (arachis) cake, decorticated	9·0	10·0	51·0	21·3	3·5	5·2	1·3
Do., do., undecorticated	8·7	8·2	32·0	24·6	21·5	5·0	1·5
Linseed-cake	11·5	11·0	28·0	34·5	8·5	6·5	1·0
Sunflower-seed cake	7·0	10·0	30·5	24·5	21·0	7·0	1·0
Poppy-seed cake	10·5	8·5	38·5	20·5	9·0	13·0	1·3
Rape cake	10·5	10·0	33·0	29·8	9·0	7·7	2·0
Sesamé cake	9·0	12·0	39·0	23·0	5·0	12·0	2·0
Beans, English	14·0	1·5	25·5	49·5	6·5	3·0	—
Peas, do.	14·0	1·7	22·5	53·3	5·5	3·0	—
Cocoanut (copra) cake	9·0	10·0	21·0	42·5	12·0	5·5	0·3
Palm kernel cake or meal (pressed—not solvent-extracted)	10·0	9·0	16·0	41·2	20·0	3·8	—
Do., do., solvent-extracted	10·0	1·8	17·4	45·0	21·7	4·1	—
Dried brewers' grains	10·0	7·0	20·0	42·5	16·0	4·5	—
Wet do. do.	76·0	1·8	5·3	11·4	4·3	1·2	—
Wheat bran	13·0	4·0	14·0	55·5	8·0	5·5	—
Do. pollards	13·0	5·0	16·0	57·0	5·0	4·0	—
Do. middlings	12·0	4·0	16·0	61·0	4·0	3·0	—
Wheat	13·5	1·9	12·0	68·9	1·9	1·8	—
Oats	13·5	4·5	11·5	58·5	9·0	3·0	—
Rye	13·4	1·7	11·5	69·5	1·9	2·0	—
Barley	14·3	2·5	11·0	65·2	4·5	2·5	—
Maize	13·0	4·5	10·0	69·6	1·5	1·4	—
Rice meal or rice bran, Rangoon	8·5	15·5	12·5	48·7	6·0	8·8	1·8
Do., do., English	10·0	10·0	11·5	54·0	6·5	8·0	2·4
Fish meal	14·0	5·5	55·0	—	·5	25·0[1]	
Dried yeast	7·4	1·0	45·5	33·9	2·2	10·0	

[1] Chiefly calcium phosphate and a little salt.

Average or Typical Composition of Moist or Bulky Farm Fodders.[2]

—	Moisture	Oil or fat	Nitrogenous substance		Digestible carbohydrates[1]	Fibre	Mineral matter (ash)
			Albuminoid	Non-albuminoid			
Pasture grass	76·7	0·9	2·9	1·1	10·9	5·2	2·3
Clover (about to flower)	81·0	0·7	2·6	0·8	8·1	5·2	1·6
Meadow hay, rich	15·0	2·3	10·2	1·8	39·5	24·0	7·2
,, ,, medium	15·0	2·2	8·0	1·2	42·0	25·4	6·2
,, ,, poor	14·0	2·0	6·3	0·5	41·1	31·0	5·1
Clover hay, medium	16·0	2·5	10·5	2·5	37·2	25·0	6·3
Oat straw	14·5	2·0	4·0		37·0	36·8	5·7
Wheat straw	13·6	1·3	3·3		39·4	37·1	5·3
Barley straw	14·2	1·5	3·5		39·1	36·0	5·7
Bean straw	18·4	1·1	8·1		31·0	36·0	5·4
Pea straw	13·6	1·6	9·0		33·7	35·5	6·6
Maize, silage	79·1	0·8	1·0	0·7	11·0	6·0	1·4
Mangolds, large	89·0	0·1	0·4	0·8	7·7	1·0	1·0
,, small	87·0	0·1	0·4	0·6	10·2	0·8	0·9
Swedes	89·3	0·2	0·7	0·7	7·2	1·1	0·8
Turnips	91·5	0·2	0·5	0·5	5·7	0·9	0·7
Potatoes	75·0	0·2	1·2	0·9	21·0	0·7	[illegible]
Field cabbages	85·7	0·7	1·7	0·8	7·1	2·4	1·6
Carrots	87·0	0·2	0·7	0·5	9·3	1·3	1·0

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[1] By 'digestible' is here meant dissolved by successive boiling in acid and alkali (*see Methods of analysis, infra*).

[2] Compiled chiefly from averages calculated and tabulated by R. Warington.

of truth is impeded by so many pitfalls and obstacles. Ruminants have a better power of digestion than horses, especially for fibrous foods, and in this respect horses are better digestors than pigs. The following figures, extracted from a table compiled by Kellner, show the average results obtained with ruminant animals as regards the quantity of albuminoids, fat, 'soluble' carbohydrates, and fibre, out of 100 parts of each of these constituents, when supplied in the form of the more common feeding stuffs. By 'soluble' carbohydrates are here meant those dissolved by successive boiling with dilute acid and dilute alkali, usually termed in commercial analyses 'digestible.' As the latter word would here be ambiguous, the alternative term 'soluble' is used. (In German works this item of 'soluble' carbohydrates is usually rendered as 'nitrogen-free extract.') It will be noticed that with some foods, the experiments have been too few, having regard to the difficulty of such work, to lend any very strong validity to the figures. In other cases, the number of trials engenders more confidence in the probable general truth of the average figures, but it will be seen even in these cases that the range from minimum to maximum quantities digested in the experiments averaged is sometimes wide.

Energy equivalents of feeding stuffs. The ultimate physiological value of any food constituent is largely dependent upon the quantity of potential energy producible by its oxidation in the system, or by the oxidation of the equivalent body substance that it replaces. This energy may be manifest in maintaining the heat of the

AVERAGE RESULTS OF FEEDING EXPERIMENTS ON FARM ANIMALS.

Matters digested out of 100 parts of each constituent when supplied in the feeding stuff specified in the first column (from Kellner).

—		Fat	Nitrogenous substance	'Soluble' carbohydrates	Fibre	Number of investigations
Cotton cake, decorticated	Range	93–100	84–96	44–71	0–100	14
	Average	94	86	67	28	
Cotton cake, undecorticated	Range	86–100	72–77	46–60	2–24	10
	Average	93	77	52	18	
Soya beans	Range	86–94	87–91	62–76	0–71	4
	Average	90	89	69	36	
Earth-nut (arachis) cake	Range	86–97	69–98	69–98	0–32	7
	Average	90	84	84	9	
Linseed cake	Range	86–97	80–90	60–96	0–92	14
	Average	92	86	78	32	
Sunflower-seed cake	Average	88	90	71	30	4
Poppy-seed cake	Average	92	79	64	61	3
Rape cake	Range	60–94	65–92	66–85	0–34	7
	Average	79	81	76	8	
Beans	Range	56–100	77–100	82–100	0–99	30
	Average	83	87	91	58	
Peas	Range	55–75	83–90	93–94	26–66	4
	Average	65	86	93	46	
Sesamé cake	Average	90	90	56	31	4
Cocoanut (copra) cake	Range	96–100	75–84	80–86	54–73	5
	Average	97	78	83	63	
Palm-kernel meal	Range	94–100	72–77	75–79	25–54	3
	Average	98	75	77	39	
Dried brewers' grains	Range	81–93	63–78	51–67	19–77	19
	Average	88	71	60	48	
Wet „ „	Range	84–89	71–74	56–74	33–45	12
	Average	86	73	62	40	
Wheat bran	Range	51–100	51–100	40–88	0–58	71
	Average	71	79	71	26	
Oats	Range	63–100	67–94	65–94	2–47	45
	Average	80	76	76	28	
Barley	Range	78–100	63–77	87–96	—	4
	Average	89	70	92	—	
Maize	Range	81–99	58–84	87–100	46–100	23
	Average	89	72	95	58	
Rice meal or rice bran	Range	82–87	48–65	67–92	0–51	14
	Average	85	57	80	15	
Pasture grass (April—May)	Range	63–68	71–79	75–84	70–75	4
	Average	66	75	79	73	
Meadow grass (June)	Average	62	70	75	66	2
„ „ (October)	Average	46	56	61	62	4
Meadow hay, rich	Range	45–68	60–73	58–76	53–80	48
	Average	57	65	68	63	

AVERAGE RESULTS OF FEEDING EXPERIMENTS ON FARM ANIMALS—*continued.*

—		Fat	Nitrogenous substance	'Soluble' carbohydrates.	Fibre.	Number of investigations
Meadow hay, medium	Range	—	49–67	53–73	50–71	104
	Average	51	57	64	59	
„ „ poor	Range	—	35–61	49–65	46–64	34
	Average	49	50	59	55	
Clover hay, best	Range	44–74	56–71	63–76	38–54	19
	Average	63	65	70	49	
„ „ medium	Range	33–63	48–59	57–69	38–52	46
	Average	53	54	64	46	
Oat straw	Range	14–51	12–50	33–55	42–66	11
	Average	36	33	46	54	
Wheat straw	Range	17–44	0–26	29–40	42–59	10
	Average	31	4	37	50	
Barley straw	Range	35–43	17–27	38–57	53–58	7
	Average	39	25	53	54	
Bean straw	Range	49–60	45–54	64–73	34–53	5
	Average	57	49	68	43	
Pea straw	Average	46	60	64	52	2
Green maize plant	Average	72	65	73	67	16
„ „ „ as silage	Range	65–90	22–67	55–77	56–83	25
	Average	80	51	67	71	
Mangolds	Range	?	44–89	91–100	0–43	22
	Average		70	95	37	
Swedes	Average	93	62	99	?	2
Turnips	Range	?	57–90	88–97	0–100	10
	Average		73	92	51	
Potatoes	Range	?	23–88	82–99	?	30
	Average		51	90		
Cabbages	Average	84	80	95	74	2

body, or in the mechanical work effected in the various movements of the body, including locomotion, the pulsation of the heart and circulation of the blood, and the mechanism of respiration Not a little of the energy latent in coarse fodder is expended in the mere work of mastication and the other mechanism of digestion. The excess of digested food over that portion spent in maintaining the temperature and effecting the movements incidental to quiescent existence, is stored up as body increase (as in a fattening ox) or used in the production of the fœtus or of milk (as in the case of a cow). In the case of a working animal, such as a horse, the excess of food digested is spent in the production of external mechanical work, such as traction; and so, of course, with a ploughing ox. The ultimate potential energy of a food-stuff is measurable by the heat generated by its complete combustion in oxygen, now usually determined for experimental purposes by burning a weighed quantity of the material with compressed oxygen in a steel bomb immersed in a known weight of water, and measuring the rise of temperature imparted to the water. Expressing the results of such determinations in large calories (a large calorie being the heat necessary to raise 1 litre of water 1 degree centigrade), the combustion of 1 gram of each of the following food constituents is found to give approximately heat as under:—

Oil or fat	9·4
Proteins	5·8
Starch or cellulose	4·1
Cane sugar	4·0
Dextrose or glucose	3 8
Milk sugar	3·9
Asparagine	3·4

In the consumption of feeding stuffs by animals, only a portion of the theoretical potential energy, as indicated by their combustion heat, is realised. In the first place, as we have already seen, only a fractional part of the food is digested, and only the digestible part can yield energy. Furthermore, the oxidation of the digested matter is incomplete. The oxidation of completely utilised proteins goes no farther than the production of urea, and, although the great bulk of the carbon of utilised food is exhaled in the completely oxidised form of carbonic acid, a portion is also given off in the unoxidised form of hydrocarbon gas or methane. In order to ascertain the energy either actually realised or potentially stored by the animal from a given diet, it is necessary to feed it in a respiration chamber fitted with such appliances that the fæces and urine can be separately collected, and the whole of the gases expired during the experiment collected and analysed. The heat or combustion equivalent of the food consumed is determined on accurately sampled portions of the daily diet. A similar determination in the dried fæces gives, by deduction, the potential heat energy in the food actually digested. A combustion of the dried residue of the urine voided and a measurement of the carbonic acid and water produced by combustion of the dried unoxidised gases exhaled from the lungs and otherwise, give the data for deducting the fuel energy corresponding to these factors, and so the real or potential energy generated or stored in the animal is determined.

In order to trace the disposition of this energy, it is necessary, in addition to the foregoing determinations, to weigh accurately the water as well as the dry food consumed, and to determine accurately all moisture given off by the animal in fæces, urine, breath, and perspiration, and also the carbonic acid evolved. By means of delicately constructed respiration calorimetric chambers, it is possible to make very exact determinations of the actual heat produced in or by the animal during the experiment, and from the whole of the data obtainable to calculate, not only what fraction of the total proteids, fat, and carbohydrates has been digested, but how much of them has been stored up in the form of flesh or fat, and how much is expended in what may be called maintenance energy and heat production. Some foods, such as hay, and especially straw, require so much energy for their mastication and digestion that only a relatively small portion of the actually digested matter may be available for increase of tissue or fat formation, or for the production (in a horse) of external work, a comparatively large quantity of heat being produced. In concentrated, easily digestible foods, the loss of energy between administration of the food and storage as flesh or fat is much less. Thus, Kellner has shown that, in the case of a fattening ox, only 41 p.c. of the potential energy in a pound of digested starch is lost or used in converting that which corresponds to the remainder into fat or other tissue. In the digested portion of meadow hay, the loss of energy involved in digestion and assimilation was over 58 p.c.; in that of oat straw, 62·4 p.c.; and in that of wheat straw, as much as 82 p.c. Similarly, Zuntz found in the case of the horse that only from 10 to 15 p.c. of available energy was consumed in the processes of digestion and assimilation in the case of maize, beans, and oats, the remainder being available for the performance of external mechanical work, while in the case of hay, the mere process of digestion and assimulation of the digestible portion consumed from 50 to 60 p.c. of the potential energy of such portion, leaving only from 40 to 50 p.c. available for 'work.' In the case of straw, the energy expended by the horse in mastication and digestion was found to be even greater than the whole of the potential energy in the portion digested, showing, apparently, that straw has a negative food value for horses, except as a 'filler' and diluent for more concentrated food.

Albuminoid ratio. By this term is meant the ratio of digestible protein or albuminoids to the digestible fat and digestible carbohydrates in the food. In order to state this on a uniform basis, fat is converted into its approximate equivalent in digestible carbohydrates by multiplying the fat by the factor 2·3, on the assumption that on the average the energy and fat-producing value of the latter is approximately 2·3 times that of the former. Thus, if a food contains 20 p.c. of digestible albuminoids, 10 p.c. of digestible fat, and 40 p.c. of digestible carbohydrates, the albuminoid ratio would be 20 : (10×2·3+40), or 20 : 63, or approximately 1 : 3. Linseed cake has an albuminoid ratio of about 1 : 2, which is called a 'narrow' ratio; and maize of about 1 : 10, which is called a 'wide' ratio; while in mangolds the ratio is exceedingly wide, namely, about 1 : 85. The efficacy of a mixed diet for a specific purpose is much affected by its albuminoid ratio. Fattening or working animals get on well with a diet of a fairly wide ratio, such as from 1 : 8 to 1 : 10, though even in the case of fattening animals, the ratio should be narrower (1 : 5 or 1 : 6) in the early stages of feeding. Young growing animals, animals with young, and cows in milk, need a diet of correspondingly 'narrow' ratio, *i.e.* richer in proteids, such as 1 : 5.

The subject of the maintenance value, energy value, and productive value of the various feeding stuffs cannot be further pursued here. It may be advantageously studied in very thorough detail in The Principles of Animal Nutrition, by H. P. Armsby, of the Pennsylvania State Agricultural Experiment Station (English publishers, Chapman & Hall, Ltd., 1903). Readers may also be referred to Chemistry of the Farm, by R. Warington (Vinton & Co., Ltd., London, 1902); to The Feeding of Crops and Stock, by A. D. Hall (John Murray, London, 1911); and to Goodwin's English translation of The Scientific Feeding of Animals, by O. Kellner (Duckworth & Co., London, 1909). The last-named book contains very full tables showing the composition, digestibility, and energy values of most of the foods in use on the farm, and ration tables for the dieting of farm animals, compiled from the results of scientific investigation. A useful table, compiled by A. Smetham and F. Robertson Dodd, showing the composition of a large range of feeding stuffs met with in commerce, including many materials not commonly offered as such to farmers, but in extensive use for the manufacture of compound foods, may be found in a paper reprinted from the Journal of the Royal Lancashire Agricultural Society for 1921, and published by that Society at Liverpool, under the title of The Valuation of Feeding Stuffs. A pamphlet on the Composition and Nutritive Value of Feeding Stuffs by T. B. Wood and E. T. Halnan is also issued from the Animal Nutrition Institute of Cambridge University, and published by the Cambridge University Press.

Analysis of feeding stuffs. The following methods are those commonly in use:—

Moisture.—A weighed quantity (usually about 3 grams) of the material, finely crushed or powdered by passing through a small mill, is dried at 100°C. until it ceases to lose weight. The loss is taken to be moisture.

Oil.—This is usually determined by extraction with ethyl ether. The method officially laid down (1908) for use under the Fertilisers and Feeding Stuffs Act in England, is as follows:—

'A weighed quantity of the sample shall be placed in a Soxhlet thimble, which shall then be placed in the Soxhlet extraction tube and extracted with washed, redistilled ether. At the end of 3 to 4 hours, the thimble shall be removed from the Soxhlet tube, dried, and its contents finely ground in a small mortar previously rinsed with ether. The substance shall then be returned to the thimble, the mortar being washed out with ether, and the extraction continued for another hour.

'After evaporation of the solvent, the oil shall be dried at 100° and weighed. The oil shall be redissolved in ether, and any undissolved matter shall be weighed and deducted.

'In the case of samples containing saccharine matter, *e.g.* sugar meals, the weighed portion in the Soxhlet thimble shall be washed twice with water, and then dried, previous to the extraction.'

A convenient quantity to work upon for determination of oil is about 3 grams.

Albuminoids.—The percentage of albuminoids, as already stated, is, for the purpose of ordinary feeding stuff analyses, conventionally arrived at by determining the nitrogen and multiplying the percentage thereof by 6·25. Nitrogen is now almost universally determined by some modification of the Kjeldahl process. The details of the method, as officially laid down (1908) for use under the Fertilisers and Feeding Stuffs Act in England, are as follows :—

'A weighed portion of the sample shall be transferred to a Kjeldahl digestion flask; 10 grams of potassium sulphate and 25 c.c. of concentrated sulphuric acid shall be added, and the flask heated until a clear liquid, colourless or of light-straw colour is obtained. The operation may be accelerated by the addition of a small crystal of copper sulphate or a globule of mercury to the liquid in the digestion flask.

'The quantity of ammonia shall be determined by distillation into standard acid after liberation with alkali, and, where mercury has been used, with the addition also of sodium or potassium sulphide solution.

'The materials used shall be examined as to their freedom from nitrogen by means of a control experiment carried out under similar conditions with the same quantities of the reagents which have been employed in the actual analysis, one gram of pure sugar being used in place of the weighed portion of the sample. The quantity of standard acid used in this control experiment shall be deducted from the total quantity of acid found to have been neutralised in the distillation of the sample.'

A convenient quantity to work upon for the nitrogen determination will, in most cases, be found to be from 1 to 1·5 grams.

The percentage of 'true albuminoids' or proteid substances, as distinguished from nonproteid bodies such as amides, &c., is sometimes determined by what is known as the phenol method, but more commonly now by the copper oxide method.

The phenol method depends upon the coagulability of proteids by phenol. A quantity of from 1 to 2 grams of the powdered feeding stuffs is covered with a warm 4 p.c. aqueous solution of phenol, to which have been added a few drops of a freshly made aqueous solution of metaphosphoric acid. After 15 minutes, a little boiling phenol solution is added, and the mixture stirred and allowed to cool. The whole is then poured on to a small filter, which is washed with more of the same liquid, but cold. After drying, the filter and its contents are transferred to a Kjeldahl digestion flask, and the nitrogen is determined as already described (Church and Kinch).

The copper oxide method depends upon the power of moist copper hydroxide to unite with proteid substances to form insoluble compounds. The preparation of cupric hydroxide used is known as Stutzer's reagent. It is made by dissolving 100 grams of copper sulphate in 5 litres of water with the addition of 2·5 c.c. of glycerol. A dilute solution of sodium hydroxide is added until the liquid is just alkaline. The precipitate of cupric hydroxide is filtered off, drained, transferred to a dish, and washed by decantation with water containing 5 c.c. of glycerol per litre, until the washings are no longer alkaline. The precipitate is mixed in a mortar with water containing 10 p.c. of glycerol, and transferred to a stoppered bottle. A gelatinous mixture is thus obtained which, when shaken up, can be removed by means of a pipette. The determination of albuminoid nitrogen is made as follows : About 1 gram of the feeding stuff is weighed out, mixed with 100 c.c. of water and boiled or heated in the water-bath for 10 minutes. A quantity of the cupric hydroxide paste, containing about 0·8 gram of actual cupric hydroxide, is added, and the whole thoroughly stirred, warmed for a short time, and allowed to cool. When cold it is filtered and washed with cold water. After drying, the filter and its contents are transferred to a Kjeldahl digestion flask, and the nitrogen determined as above described. Instead of adding the cupric hydroxide paste directly to the solution, it is desirable to place the requisite quantity in a separate beaker, treating it with cold water, allowing it to settle, and pouring off the water in order to eliminate the glycerol, which is used merely as a vehicle for the preservation of the reagent.

Fibre.—A weighed quantity (conveniently about 3 grams) of the ground sample, either with or without previous extraction with ether, is boiled for half an hour with 125 c.c. of a 2 p.c. solution of sulphuric acid, the loss of water due to boiling being continuously made up. The fluid is diluted with a few hundred cubic centimetres of water, and allowed to stand for some time. The bulk of the fluid is then filtered off, any matter that becomes transferred to the filter being washed back again into the original vessel. The residue is then boiled with 125 c.c. of a 2 p.c. solution of potassium hydroxide, diluted, and filtered—this time through counterpoised filters. The fibrous matter is washed on to the filter, washed with boiling water until the washings are no longer alkaline, then with a little dilute acid, and then with water until the washings are no longer acid. It is next washed several times with methylated spirit, and, if the oil was not removed prior to the fibre determination, it must be finally washed several times with ether. Finally the fibre is dried to constancy in a water-oven, and weighed.

Ash.—A quantity of the material (for example, 3 grams) is placed in a platinum capsule and heated over an argand burner turned down low. The heating is continued over a yellow flame until the residue is free from carbon. The residue under incineration should be stirred from time to time with a platinum wire, being meantime lightly covered with an arched piece of platinum foil. Ignition over a Bunsen burner is more rapid, but is liable to result in loss of potash.

Sand and other silicious matter.—The ash, after being weighed, is digested in the platinum basin with a little dilute hydrochloric acid, and the silicious matter filtered off, ignited, and weighed. This consists of sand, together with —in the case of some foods—silica derived from naturally silicious tissues, such as rice husks.

'*Digestible,' carbohydrates.*—This item, which includes starch, sugars, mucilaginous matter, pentosan derivatives, and other bodies—sometimes also termed 'soluble carbohydrates' or, as in Germany, 'nitrogen-free extract'—is taken by difference. For the methods of determining the various sugars, starch, &c., separately, the reader is referred to other sections of this work. B. D.

FELSPAR or Feldspar. (Fr. *Feldspath*; Ger. *Feldspath*, *Feldspat*; from the Swedish *Feltspat* or *Fältspat*, meaning 'field-spar.') A large isomorphous group of important rock-forming minerals consisting of alumino-silicates of alkalis (potassium and sodium, rarely rubidium, cæsium, and lithium) and alkaline earths (calcium, and less often barium). They include polysilicates or trisilicates of the type $R'AlSi_3O_8$, and orthosilicates of the type $R''Al_2(SiO_4)_2$. The principal molecules representing the end-members of the isomorphous series are $KAlSi_3O_8$ (Or=orthoclase), $NaAlSi_3O_8$ (Ab=albite), and $CaAl_2Si_2O_8$ (An=anorthite). Others of less importance, or whose existence is only assumed on theoretical grounds, are $BaAl_2Si_2O_8$ (Ce =celsian), $Na_2Al_2Si_2O_8$ (Cg=carnegieite), and $RbAlSi_3O_8$ (rubidium-microcline).

The felspars are usually divided crystallographically into two series, the monoclinic (or oblique) felspars and the triclinic (or anorthic) felspars. But, although these belong to different systems of crystallisation, they resemble one another closely in habit, cleavage, and general crystallographic characters. An important feature of all felspars is the existence of good cleavages in two directions; the more perfect one being parallel to the basal pinakoid $c(001)$, whilst the second is parallel to the clinopinakoid or plane of symmetry $b(010)$ in the monoclinic felspars, and parallel to the corresponding brachypinacoid $b(010)$ in the triclinic felspars. In the monoclinic system these two cleavages are necessarily at right angles (90°), and the felspars belonging to this system are consequently described as orthoclastic felspars; whilst in the triclinic system the cleavage angle *bc* varies slightly from a right angle (in anorthite *bc* =85° 50′, and in albite *bc*=86° 24′), and for this reason these felspars are called plagioclastic felspars, or simply plagioclase. To these two series may be added a third—pseudo-monoclinic series—the members of which are shown by their optical characters to be triclinic, but in the external form of their crystals they do not differ from those of the monoclinic series and the cleavage angle *bc* does not differ appreciably from 90°. The several members of these three series of felspars are set out in the following table:—

	Monoclinic series	Pseudo-monoclinic series	Triclinic series
$KAlSi_3O_8$	Orthoclase	Microcline	—
$mKAlSi_3O_8$ $nNaAlSi_3O_8$	Soda-orthoclase	Anorthoclase	—
$NaAlSi_3O_8$	Barbierite	Cryptoclase	Albite
$mNaAlSi_3O_8$ $nCaAl_2Si_2O_8$	—	—	Oligoclase, Labradorite, &c.
$CaAl_2Si_2O_8$	—		Anorthite
$Na_2Al_2Si_2O_8$	—	—	Carnegieite
$BaAl_2Si_2O_8$	Celsian	—	—
$mBaAl_2Si_2O_8$ $nKAlSi_3O$	Hyalophane	—	—

The only members of practical importance are the potash-felspars, orthoclase, and microcline (which, as noted below, are perhaps really identical); the soda-felspar, albite; the lime-felspar, anorthite; and the soda-lime-felspars, oligoclase, andesine, labradorite, and bytownite. All of these, with the exception of potash-felspar, belong to the isomorphous group of plagioclase-felspars, of which albite and anorthite are the end-members. The limits of composition usually assigned to these are:

			SiO_2	Al_2O_3	Na_2O	CaO
Plagioclase-felspars.	Albite	Ab_1An_0	68·7	19·5	11·8	—
	Oligoclase	Ab_8An_1	64·9	22·1	10·0	3·0
	Andesine	Ab_3An_1	62·0	24·0	8·7	5·3
	Labradorite	Ab_1An_1	55·6	28·3	5·7	10·4
	Bytownite	Ab_1An_3	49·3	32·6	2·8	15·3
	Anorthite	Ab_1An_6	46·6	34·4	1·6	17·4
		Ab_0An_1	43·2	36·7	—	20·1

A character which always enables the plagioclase-felspars to be readily recognised is the invariable presence of lamellar twinning according to the albite-law. This is shown in thin sections of rocks when examined in polarised light by the banding due to the different directions of extinction in alternate lamellæ. In a hand-specimen it is shown on the basal plane $c(001)$, and on the perfect cleavage parallel to this face, by a system of fine striæ parallel to the edge of intersection of the two cleavages. These striæ can usually be detected with the aid of a pocket-lens when the cleavage surface is held at a suitable inclination to the light; and two sets of reflections can be obtained in albite inclined at 7° 12′, and in anorthite at 8° 20′. Albite-twinning is not present in orthoclase, but is present in microcline, though in this case the striæ are not evident on the cleavage surface. This difference often affords a ready means of distinguishing at sight a potash-felspar from a soda-lime-felspar. In microcline there is also a second lamellar twinning according to the pericline-law, which, in conjunction with the lamellar albite-twinning, produces a very characteristic cross-hatched structure, sometimes to be seen on the basal plane of crystals, but very evident when thin sections are examined in polarised light; this being, indeed, often the only means of distinguishing microcline. Several other twin-laws have been described for the felspars, the important ones being the Carlsbad, Baveno, and Manebach types. The very common occurrence of repeated twinning in this group of minerals gives rise to the suggestion that the higher degree of symmetry in the monoclinic series is merely the result of twinning, and that all felspars are really triclinic. This is obviously the case in the pseudo-monoclinic series, in which, on optical examination, the twinning is seen to be repeated on a very minute scale. If this became ultra-microscopic, then the crystal could not be distinguished from a true monoclinic crystal. The crystallographic grouping shown in the above table would then break down, while the chemical grouping alone stands. Microcline would then be identical with orthoclase, which, indeed, it is in density, refractive indices, mode of occurrence, and its practical applications.

Some of the constants of the three most important species of felspar are given below :—

	Orthoclase ($KAlSi_3O_8$)	Albite ($NaAlSi_3O_8$)	Anorthite ($CaAl_2Si_2O_8$)
	p.c.	p.c.	p.c.
SiO_2	64·7	68·7	43·2
Al_2O_3	18·4	19·5	36·7
CaO	—	—	20·1
K_2O	16·9	—	—
Na_2O	—	11·8	—
Sp.gr.	2·56	2·62	2·76
Hardness	6–6½	6–6½	6 6½
Melting-point . .	1150° c.	1100° c.	1550°
Specific heat . .	0·187	0·197	0·197
Cleavage angle (*bc*) .	90°	86° 24′	85° 50′
Optical extinction on *c*	0°	+4°	−37°
,, ,, *b*	+5°	+19°	−36°
Ref. Index (Na) α .	1·519	1·529	1·576
,, ,, β .	1·523	1·533	1·583
,, ,, γ .	1·524	1·539	1·588
Birefringence γ–α .	0·005	0·010	0·012

The recognition of a mineral as felspar is usually evident by the cleavages, dullness of colour and lustre, hardness, resistance to acids, &c.; but the discrimination of the several species is not always so easy. The optical characters of cleavage flakes afford a useful guide, and the specific gravity of fragments can be readily determined in a heavy liquid with the aid of indicators. J. Szabó (Ueber eine neue Methode die Feldspathe auch in Gesteinen zu bestimmen, Budapest, 1876; *v.* G. A. J. Cole, Aids to Practical Geology, 5th ed. London, 1906, 78-85) devised a method in which the intensity of coloration imparted to the Bunsen flame gives an approximate indication of the percentage of potassium and sodium present. Anorthite is decomposed by hydrochloric acid with separation of gelatinous silica. The other felspars are only very slightly attacked by acids (except hydrofluoric), alkaline solutions, and carbonated water; but they are decomposed by hot alkaline solutions under pressure.

The following analyses are of: I, Orthoclase from Norway, as used in the manufacture of porcelain; formula $Or_{78}Ab_{22}$. II, Microcline (amazon-stone) from Antaboka, Madagascar, $Or_{71}Ab_{27}An_2$. III, Albite from Amelia Co., Virginia, $Ab_{98}Or_2$. IV, Oligoclase (sun-stone) from Tvedestrand, Norway, $Ab_{71}An_{22}Or_7$. V, Labradorite from Ardglass, Co. Down, $Ab_{33}An_{62}Or_5$. VI, Anorthite from Vesuvius, $Ab_4An_{94}Or_2$.

	I	II	III	IV	V	VI
SiO_2 .	64·98	63·55	68·44	61·30	52·33	43·96
Al_2O_3 .	19·18	18·55	19·35	23·77	30·22	35·30
Fe_2O_3 .	0·33	0·34	—	0·36	0·40	0·63
CaO .	trace	0·36	—	4·78	12·52	18·98
MgO .	0·25	0·10	—	—	—	0·45
K_2O .	12·79	13·90	0·43	1·29	0·85	0·40
Na_2O .	2·32	3·30	11·67	8·50	3·62	0·47
Ign. .	0·48	—	—	—	0·36	—
	100·33	100·10	99·89	100·00	100·30	100·19
Sp.gr. .	—	2·58	2·61	2·66	2·71	2·76

Felspars are of wide distribution, according to F. W. Clarke forming about 56 p.c. of the earth's crust. They occur as primary constituents in igneous rocks of nearly all kinds, and are abundant in gneisses and metamorphic rocks. The alkali-felspars occur preferably in the more siliceous rocks (granite, &c.), whilst lime-felspars are more common in basic rocks (gabbro, basalt, &c.). Anorthite is also found in certain types of meteoric stones. Felspars are very susceptible to alteration, being attacked by carbonated, acid, and alkaline waters, and they give rise to a great variety of secondary minerals. By the action of weathering processes the alkalis and lime generally pass into solution, remaining partly in the soil, and in part being removed in solution to form eventually secondary deposits of salts and limestone; whilst kaolin and free silica remain behind to give rise to deposits of clay.

All the naturally-occurring felspars have been prepared artificially, and in addition others containing strontium, barium, and lead in place of calcium, or potassium in place of sodium in the plagioclases. The basic felspars crystallise readily and are easily obtained by dry fusion; but the alkali-felspars form extremely viscous glasses, and have not been crystallised by dry fusion without fluxes. Much experimental work has been done in connection with the isomorphism of the felspars and in rock synthesis (*v.* F. Fouqué and A. Michel-Lévy, Synthèse des Minéraux et des Roches, Paris, 1882; A. L. Day and E. T. Allen, The Isomorphism and Thermal Properties of the Feldspars, Carnegie Inst., Washington, 1905).

For practical purposes the felspars find applications in several directions. Some are used as gem-stones and ornamental stones. As a rule, these minerals are dull in colour, cloudy, and imperfectly transparent, but certain varieties exhibit special optical and colour effects. *Moon-stone*, a variety of orthoclase obtained mainly from Ceylon, displays a soft bluish milky sheen (glaucescence). Somewhat similar, but with brighter colours, is *peristerite* (named from περιστερά, a pigeon, on account of the colours resembling those on a pigeon's neck), a variety of albite from Ontario. *Sunstone*, or avanturine felspar, exhibits a metallic spangled effect, due to the enclosure of scales of hæmatite; this is best shown in the oligoclase from Tvedestrand in Norway, but is also met with in some other felspars. *Labradorite* in certain specimens, particularly those found abundantly as boulders on the coast of Labrador, though of a dull dark-grey colour, yet at just a particular angle with respect to the incident light they suddenly shine up with brilliant metallic colours. This change of colour or labradorescence is due to the interference of light caused by numerous minute enclosures in the mineral. The same effect is also shown by the anorthoclase in the augite-syenite (laurvikite) from Laurvik and Fredriksvärn in the south of Norway, a rock much used as a polished ornamental stone. A clear transparent oligoclase from Mitchell Co., North Carolina, has been cut in the brilliant form as a gem. *Amazon-stone* (*q.v.*) is a green microcline. (On the use of felspar as gem-stones, *v.* M. Bauer, Precious Stones, transl. by L. J. Spencer, London, 1904.)

The chief use of felspar in the industrial arts is for the manufacture of porcelain and enamel ware of all kinds, including electrical goods. For this purpose only an alkali-felspar, preferably potash-felspar or a potash-soda-felspar, is employed; the lime-felspars not being suitable, since they readily crystallise. In the finest porcelain, felspar (10-35 p.c.) is added to the body, and as it fuses it firmly binds the particles of clay and quartz; but it is chiefly for the glaze that felspar (30-50 p.c.) is added. The best quality is used for making artificial teeth. Small amounts are used by glass manufacturers, especially for producing an opalescent glass. Fused felspar forms a firm bond for emery, corundum, and carborundum wheels.

As an abrasive, felspar is especially suitable for certain purposes. Owing to its cleavage, it powders to angular fragments; and its hardness is about the same as that of glass. It is therefore used as a cleaner and polisher of glass articles, and forms an ingredient of scouring soaps. Any felspar serves this purpose, so long as it is free from quartz. Labradorite from Duluth, Minnesota, is used as a sandpaper in wood-working. Other minor uses of felspar are the manufacture of tarred roofing material, for surfacing concrete, and as a poultry grit.

A great variety of processes have been devised and patented for utilising felspar as a source of potash (*q.v.*), but these have not been able to compete with the slowly-acting geological processes which produced the Stassfurt deposits from the same material. Ground felspar used directly as a fertiliser is slow in its action, but lasting.

Commercial felspar is all obtained by quarrying veins of granite-pegmatite. This is a very coarse-grained rock consisting of alkali-felspar, quartz, and mica, together with small amounts of tourmaline, beryl, and various rare minerals. The same quarries are sometimes worked also for quartz and mica; those of California, Maine, Connecticut, and Madagascar yield gem-stones; and those of southern Norway small amounts of rare-earth minerals, *e.g.* monazite, gadolinite, euxenite, &c. The felspar is, as a rule, orthoclase or microcline; but veins of soda-pegmatite, consisting mainly of albite with a little hornblende, are worked in Pennsylvania, Maryland, and at Villeneuve in Quebec. The largest producer is the United States, principally along the Appalachian Mountains in the eastern States, and in California. (*v.* E. S. Bastin, Economic Geology of the Feldspar Deposits of the United States, U.S. Geol. Survey, Bull. 420, 1910; A. S. Watts, Mining and Treatment of Feldspar and Kaolin in the Southern Appalachian Region, U.S. Bureau of Mines, Bull. 53, 1913; A. S. Watts, The Feldspars of the New England and North Appalachian States, *ibid.* Bull. 92, 1916; F. J. Katz, annual reports in Mineral Resources, U.S. Geol. Survey.) In Canada the principal quarries are in Frontenac Co., Ontario. Other large producing countries are Norway, Sweden, and Italy. The spar should be free from iron-bearing minerals and mica, but the presence of 15–20 p.c. of quartz is not injurious for pottery. It is sometimes calcined before being finely ground and screened.

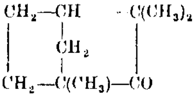
In the British Isles there is abundance of available material in the pegmatite-veins traversing the ancient gneisses of Sutherlandshire. The average amount of potash in the microcline of this district is 12·8 p.c., and for the whole rock 6·7 p.c. A few smaller pegmatite-veins are present in Cornwall; and the well-known Cornish china-stone is rich in partly altered felspar. The discovery of a vein of red felspar at Belleek in Co. Fermanagh led to the establishment of porcelain works at this locality. The red felspar becomes white on calcination, the iron passing into the condition of magnetite, the particles of which may be removed by means of a magnet. Other Irish occurrences are known in Co. Mayo and Co. Donegal. The abundantly occurring granites of Cornwall, Scotland, and Ireland contain, on an average, about 5 p.c. of potash, a portion of which is, however, carried in the mica. (*v.* Special Reports on the Mineral Resources of Great Britain, Mem. Geol. Survey, vol. v. 1916, 2nd edit., 1917; P. G. H. Boswell, British Supplies of Potash-Felspar, considered from the Glass-Making point of view, J. Soc. Glass Technology, 1918, ii. 35–71).

L. J. S.

FENCHENE *v.* FENCHONE.

FENCHONE $C_{10}H_{16}O$. A ketone isomeric with camphor. It is optically active, *d*-, *l*-, and *r*- fenchone all being known. *d-Fenchone* was discovered by Wallach in fennel oil. The fraction boiling at 190°–195° is treated with three parts of concentrated nitric acid to oxidise anethol and other impurities. The product is poured into water, the separated oil being washed with caustic soda solution, distilled in steam, dried, and finally crystallised at a low temperature (Wallach and Hartmann, Annalen, 259, 324; Wallach, *ibid.* 263, 129). *d*-Fenchone also occurs in small quantities in Russian oil of anise (Bourchardat and Tardy, Bull. Soc. chim. [iii.] 16, 616; Compt. rend. 1896, 122, 624)

Pure fenchone is a colourless oil, b.p. 192°–193°; sp.gr. 0·9465 at 19°; prolonged cooling at low temperatures causes it to solidify to large crystals, m.p. 5°–6°; $\mu_D=1{\cdot}46306$ at 19°, molec. ref.$=44{\cdot}23$; $[\alpha]_D+71{\cdot}97°$. It is not oxidised in the cold by nitric or sulphuric acids, but potassium permanganate converts it into dimethylmalonic, oxalic, and acetic acids. By heating it for six days with concentrated nitric acid, there are formed dimethylcarballylic, dimethylmalonic, *iso*camphoronic, *iso*butyric, and acetic acids, together with a nitrofenchone (Gardner and Cockburn, Chem. Soc. Trans. 1898, 708; Semmler, Chem. Zeit. 1905, 29, 1213; *cf.* Konowaloff, J. Russ. Phys. Chem. Soc. 1903, 35, 953); and by heating with sulphuric acid at 80°, 4-aceto-1:2-xylene is formed (Marsh, Chem. Soc. Trans. 1899, 1058). Warming with phosphorus pentoxide yields *m*-cymene, b.p. 175°–176° (Wallach, Annalen, 275, 157). Reduction by sodium in amyl alcohol or treatment with phthalic anhydride yields *l-fenchyl* alcohol $C_{10}H$[illegible]OH; m.p. 45°; b.p. 197°–200°; $[\alpha]_D$ $-10{\cdot}35°$ (Bertram and Helle, J. pr. Chem. [ii.] 61, 293). This is converted by phosphorus pentachloride into *fenchyl chloride*, b.p. 84°–86°, which, on heating with aniline, is converted into the terpene *fenchene* $C_{10}H_{16}$, b.p. 150°–152°. A solid fenchyl chloride, m.p. 92°, has been obtained by Kondakoff from fenchyl alcohol (J. pr. Chem. 1909, [ii.] 79, 271). Fenchene has been prepared synthetically by treating nopinone and bromacetic ester with zinc and hydrolysing the hydroxy ester thus formed (Wallach, Annalen, 363, 1). Fenchene is oxidised by concentrated nitric acid, yielding *cis*-camphopyric acid and its anhydride. Phosphorus pentachloride reacts with fenchone yielding chlorfenchenephosphinic acid $C_{10}H_{14}ClPO(OH)_2$, chlorfenchene and α- and β-chlorfenchene hydrochlorides (Gardner and Cockburn, Chem. Soc. Trans. 1897, 1157; 1898, 275, 704). Ammonium formate reacts with fenchone, yielding the formyl derivative of D.*l*-fenchylamine from which the free base $C_{10}H_{17}NH_2$ is easily obtained: b.p. 195°; sp.gr. 0·9095; $[\alpha]_D$ −24·63°. Sodium nitrite and acetic acid react with fenchylamine, producing D.*l*-fenchene, an isomeric hydrocarbon, *d*-limonene and cineol (Wallach, Annalen, 362, 174). D.*l*-fenchene, when warmed with acetic and sulphuric acids, yields *iso*fenchyl alcohol, b.p. 201°-202°, which, on oxidation with chromic acid, yields *iso*fenchone $C_{10}H_{16}O$, b.p. 201°, sp.gr. 0·943 at 18·5°, $[\alpha]_D$ +9° 35'. By heating fenchone and bromine in a sealed tube for 24 hours, bromofenchone, b.p. 131°–134° (18 mm.), is obtained. Alcoholic potash converts bromofenchone into γ-fencholenic acid, which on being dissolved in concentrated sulphuric acid and poured on to ice, yields an isomeric compound, m.p. 77°; three fencholenic acids are known (Wallach, Annalen, 315, 273; Chem. Zentr. 1899, ii. 1052; Czerny, Ber. 1900, 2287; Balbiano, Gazz. chim. ital. 1900, 30, ii. 382; Semmler and Bartelt, Ber. 1906, 3960; 1907, 432). Like camphor, fenchone reacts with sodium, forming a pinacone $C_{20}H_{34}O_2$, b.p. 219° (13 mm.), m.p. 97°. The constitution of fenchone is still under discussion, but the evidence available seems to indicate the following formula:—

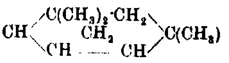


(Wallach, Annalen, 369, 63; Semmler, Ber. 1907, 4591; Bouveault and Levallois, Compt. rend. 1908, 146, 180; *cf.* Glover, Chem. Soc. Trans. 1908, 1285).

l-Fenchone was discovered by Wallach in thuja oil. The fraction boiling at 190°–200° may be warmed with nitric acid to oxidise the thujone and then steam distilled or better be oxidised with potassium permanganate to destroy the thujone and then treated with semicarbazide hydrochloride, which reacts with the *l*-camphor, which is also present more quickly than with the *l*-fenchone, and forms an effective agent for separating them (Wallach, J. Pharm. Chim. 1896, 3, [9] 465; Chem. Zentr. 1905, ii. 675; Annalen, 353, 209). *l*-Fenchone has b.p. 192°–194°, m.p. 5°, $[\alpha]_D$ −66·94°, and forms a series of derivatives similar to those obtained from *d*-fenchone. For *r-fenchone* and its derivatives, *v.* Bouveault and Levallois, Compt. rend. 1909, 148, 1399, 1524.

For further references to fenchone and derivatives, *v.* Wallach, Annalen, 284, 324; 300, 294; Semmler, Ber. 1906, 2577; Mahla, Ber. 1901, 3777; Rimini, Gazz. chim. ital. 1909, 39, ii. 196; Bouveault and Levallois, Bull. Soc. chim. 1910, [iv.] 963, 968; Nametkin, J. Russ. Phys. Chem. Soc. 1915, 47, 1590; Qvist, Ann. 1918, 417, 278 (*v.* KETONES).

FENCHYLENE



A volatile liquid with a faint odour recalling that of fenchene, obtained by heating methyl *iso*fenchylxanthate at 230°; b.p. 139°–140° (corr.); sp.gr. 0·8381 20°/4°; n_D=1·4494 at 20°, and $[\alpha]_D$= −68·76° (in alcohol). Combines with bromine, yields a crystalline nitrosochloride and gives *cis*-fenchocamphoric acid when oxidised with alkaline permanganate (Nametkin and Rusheneeva, J. Russ. Phys. Chem. Soc. 1916, 48, 450; J. Soc. Chem. Ind. 1917, 36, 304).

FENNEL FRUIT. *Fœniculi fructus*, B.P. The dried ripe fruit of *Fœniculum vulgare* (Mill.).

FENUGREEK. *Trigonella Fœnum græcum.* A plant possessing a characteristic flavour, used largely as a condiment for cattle.

According to analyses by D'Ancona (Landw. Versuchs-Stat. 1899, 51, 387), the dry matter contains—

Protein	Fat	N-free extract	Crude fibre	Ash
13·4	3·4	47·0	30·6	5·6

The pure ash contained—

K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	SiO_2	Cl
19·1	7·6	29·8	1·0	4·9	8·1	4·1	23·5	1·1

In composition, fenugreek resembles crimson clover and it is recommended as a farm crop. Since, however, the peculiar flavour of the plant is transmitted to both milk and meat, the fodder is more suited for working animals than for fattening or milk production. The peculiar odour and flavour of the plant is said to be due to an oil; it is very pronounced in the spring, but becomes less when the plant ripens.

The seeds contain trigonelline $C_7H_7NO_2$, the betaine of pyridine- 2-carboxylic acid (Jahns, 1885). Among the carbohydrates in the seeds of fenugreek is a mannogalactan, which, under the influence of a soluble ferment, produced on germination, hydrolyses with the formation of reducing sugars (Bourquelot and Herissey, Compt. rend. 1900, 130, 42, and 731). H. I.

FERBERITE *v.* WOLFRAMITE.

FERGANITE. A hydrated uranium vanadate $U_3(VO_4)_2,6H_2O$, containing also a small amount of lithium. It is related to carnotite (*q.v.*), and is found as sulphur-yellow scales, together with other uranium minerals, in province Fergana, Russian Turkestan. L. J. S.

FERGUSONITE. A rare mineral consisting of columbate (and tantalate) of yttrium and cerium earths together with a small amount of uranium, the general formula being $R'''(Cb,Ta)O_4$. Tetragonal crystals were found in Greenland in 1826, but usually the mineral is massive with a lustrous, pitchy appearance on the fractured surfaces; sp.gr. 5·8. It is optically isotropic, owing to alteration and hydration: when heated, it suddenly shows an incandescent glow, becomes fractured and anisotropic, and gives off gases (helium, &c.). The mineral occurs in pegmatite-veins at Ytterby in Sweden, near Arendal and elsewhere in Norway, and in some abundance as large masses at Barringer Hill in

Llano Co., Texas. At the last-named locality, it has been mined, together with gadolinite (*q.v.*) and other rare-earth minerals, for the supply of yttrium, &c. Other localities are Coolegong in Western Australia, Madagascar, and the Caucasus. L. J. S.

FERMENLACTYL. A preparation of lactic acid bacilli.

FERMENTATION (including Enzyme Action and Chemical Action of Bacteria).

History of the development of ideas about fermentation. The phenomena of alcoholic fermentation seem to have been familiar to man from the earliest times in the processes of the production of wine, accompanied by effervescence and frothing, and of the baking of bread, accompanied by the rising of the dough. These obvious characteristics of fermentation find expression in the names applied in various languages both to the process itself (fermentation, Lat. *fervere*, to boil; *Gahrung*, from a Teutonic root, *jesen*, to froth, from which the word *yeast* is also derived) and to the agent by which it was caused (yeast, as above, leaven, *levare*, from the Lat. *levare*, to raise; *Hefe*, Ger. *heben*, to lift; referring to the rising of the scum of yeast in fermentation and the rising of the dough in baking).

The term *fermentation* was at first applied without distinction to all changes accompanied by effervescence, but after 1659 (Sylvius de la Boë) gradually became limited to alcoholic fermentation, along with such cases of acid fermentation and putrefaction as were accompanied by evolution of gas.

Further knowledge of the chemical nature of fermentation came from the experiments of Lavoisier (1789), who showed that in alcoholic fermentation, the sugar was quantitatively decomposed into alcohol and carbon dioxide (together with some acetic acid). These relations were rendered more precise by Gay-Lussac (1810), whose conclusions may be summed up in the equation of alcoholic fermentation:

$$C_6H_{12}O_6 = 2CO_2 + 2C_2H_6O$$

Fermentation was looked upon as a chemical process set up by an unknown agent, termed the ferment, produced by the oxygen of the air from the fruit juices, &c., which underwent the change, this view being founded on the observation (Gay-Lussac) that boiled grape juice only fermented after exposure to air. The process of fermentation had been regarded by Willis (1659) and Stahl (1697) as consisting in a violent internal motion of the particles of the fermenting substance set up by an aqueous liquid, a conception which was replaced by that of catalytic force by Berzelius (1839), according to which the ferment, like other catalytic agents, was found unchanged at the end of the process. Liebig (1839), on the other hand, held the view that the ferment was an unstable body which itself underwent decomposition and that it was the internal motion due to this which was transferred to the fermentable substance and brought about its decomposition. The action only persisted as long as this metamorphosis of the ferment was in progress, and came to an end when this ceased. The ferment itself was regarded, in agreement with Gay-Lussac, as being formed by the action of oxygen on the nitrogenous materials of the fermentable liquid, and the amount produced was dependent on the special nature of this, and might be, as in brewing, more than sufficient to cause the decomposition of the whole of the sugar present.

These views were founded on the belief that yeast was a chemical substance comparable to any of the well-known organic products. Even before the publication of the views of Berzelius and Liebig, however, strong evidence had been brought forward that this was not the case. As early as 1680, Leeuwenhoek had described the granular appearance of yeast under the microscope and 'animalcules' of putrefying materials had also been observed; but in spite of a few other isolated observations, it was not until about 1836 that the intervention of living organisms in fermentation and putrefaction was rendered probable. In that year, Schulze showed that infusions of various animal and vegetable materials remained free from all putrefaction, if, after they had been well boiled, they were only allowed to come in contact with air which had passed through sulphuric acid. The same thing was subsequently shown by Schwann to hold if the admitted air were heated, and the observations were extended to alcoholic fermentation. The conclusion was drawn by both these investigators that putrefaction was caused by living germs present in the air, which developed in the putrescible liquid. The microscopic examination of a fermenting sugar solution revealed the presence of yeast cells capable of reproduction by budding, and Schwann attributed to this living organism, which he named 'Zuckerpilz' (sugar fungus), the production of alcoholic fermentation. Curiously enough, almost simultaneously with Schwann, two other investigators, Cagniard-Latour in France and Kützing in Germany, came independently to the same conclusion, as the result of microscopic obervations. These conclusions were rejected by Berzelius and Liebig, who replied to them by the theories already mentioned, but, in spite of this powerful opposition, they gradually won for themselves a considerable body of adherents, especially in Germany and among those engaged in brewing (*see* Hefe, Fäulniss und Gährung, 208–229, Berlin, 1904).

The evidence in favour of this vitalistic view of the cause of fermentation was greatly strengthened by the experiments of Schröder and von Dusch (1864), who discovered the important fact, which has proved to be an almost indispensable feature of bacteriological technique, that air lost its power of producing putrefaction when it was simply filtered through cotton wool. Many difficulties, however, still remained unexplained, which prevented the universal acceptance of the vitalistic view. Milk, for example, was found to become sour after having been boiled, in spite of all precautions, and no organism could be recognised in it capable of producing the change. Moreover, other ferments existed, such as diastase (Dubrunfant, 1830; Payen and Persoz, 1833), which, like yeast, lost their power of action when heated, and yet were completely soluble in water and devoid of all trace of organisation.

The final proof that fermentative changes in general, such as the alcoholic and lactic fermentations, putrefaction, &c., were actually produced by living organisms was afforded by the classical researches of Pasteur (Compt. rend. 1857, 45, 913). Pasteur showed, in the clearest possible manner, that every fermentation was produced by a specific organism. He regarded fermentation as indissolubly bound up with the life of the organism, and summed up his conclusions in the aphorism, 'No fermentation without life.' The recognition of micro-organisms as the cause of fermentation rendered it necessary to differentiate between these so-called organised ferments and the substances, such as diastase, invertase, pepsin, &c., which had gradually become known, and which could be extracted from the higher plants and animals and even from micro-organisms, and were therefore known at first as soluble ferments, and later, following the suggestion of Kühne, as *enzymes* (ἐν, in; ζύμη, yeast).

A long discussion then arose on the question whether any essential difference existed between the modes of chemical action of these two classes of ferments. Moritz Traube (1858) formulated the theory that all chemical action of micro-organisms was due to enzymes produced in the cell of the organism, and he was supported by Berthelot, Hoppe-Seylor, and many others. Pasteur, on the other hand, maintained his original thesis, and, stimulated by his discovery (Compt. rend. 1861, 52, 344, 1260) that many micro-organisms could live in the absence of free oxygen, developed the view that fermentation was life without free oxygen, the physiological function of the process being to supply the organism with the oxygen or the energy necessary for its metabolism. Pasteur's theories, aided by his brilliant exposition and ingenious experiments, gained the day for the vitalistic view, especially as the supporters of Traube's conception were unable, in spite of many attempts, to adduce positive evidence of the isolation of an enzyme capable of producing one of the fermentations characteristic of living organisms. A middle path was taken by Nägeli, who suggested the idea that the power of producing fermentation was restricted to the living protoplasm of the cell, and consisted in the transference of a molecular vibration from this to the fermentable substance.

This theory was disproved and the original idea of M. Traube strikingly confirmed in 1897 by Eduard Buchner, who succeeded in preparing from yeast a liquid capable of fermenting sugar. It has since been shown that the lactic and acetic fermentations can also be produced in the absence of living cells. Buchner's experiments disprove the vitalistic theory as held by Pasteur, and the view is now generally adopted that micro-organisms produce chemical change by means of enzymes present in their cells. The chemical changes produced by micro-organisms are thus brought into line with those effected by the numerous and well-known enzymes secreted by the cells of various organs of the higher plants and animals as well as by micro-organisms, and the modern conception of fermentation embraces all the different changes produced by these various agents.

General properties of enzymes. It has been found that enzymes bring about chemical change by acting as catalytic agents; that is to say, they greatly increase the velocity of the particular reaction in question without themselves undergoing any permanent change. No very definite criterion of an enzyme as distinguished from a catalyst in general, exists, but the term is generally limited to catalysts formed by living organisms, and it is an almost invariable rule that enzymes in solution are thermolabile, losing their activity as a rule rapidly at 70°. In the absence of moisture, on the other hand, they are much more stable, and may be heated in some cases to 110° for a considerable time without being destroyed. In this respect, the inactivation of enzymes by heat bears a close resemblance to the heat coagulation of proteins (Chick and Martin, J. Physiol. 1910, 40, 404).

Chemically, the enzymes are presumably of a very complex character, but they have, up to the present, evaded the skill of the chemist, no one of them having been isolated in a pure condition and submitted to investigation. It appears, however, to have been established with some degree of probability that certain enzymes (pepsin, diastase) are not proteins. All enzymes appear to form colloidal solutions, and in agreement with this they only possess very slight powers of diffusion, so that they only pass slowly and imperfectly through the ordinary dialysing membranes.

Ecto- and Endo-enzymes. In many cases, the enzymes, after being elaborated in the cell, are excreted into the surrounding medium, in which they produce their characteristic effects. This is the case, for example, with some of the digestive ferments of the animal body, the ptyalin of the salivary gland, the pepsin of the stomach, the trypsin of the pancreas (in this case in an inactive form) being all poured into some portion or other of the alimentary canal. In other cases, the enzyme does not pass out of the cell, the chemical change in question taking place inside the cell. The best known case of this kind is probably that of alcoholic fermentation, which occurs entirely inside the yeast cell.

A second point of difference lies in the behaviour of enzymes towards solvents. Many enzymes (*ectoenzymes*) can readily be extracted by such solvents as water, normal saline (0·8 p.c. sodium chloride solution), and glycerol from the cells after the organism has died. Thus pepsin and chymase, the enzyme of rennet, can be extracted by weak acid or glycerol from the membrane of the stomach of the calf or other animal. Others again cannot be removed from the cell in this way until the cell wall has been ruptured, or rendered permeable by drying or treatment with reagents, and these are termed *endoenzymes* or *intracellular enzymes*. The autoclastic enzymes of the animal body are instances of this, as are also the zymase and tryptase of yeast.

Extraction of enzymes. These facts provide the clue to the practical methods adopted for the extraction of enzymes.

1. *Soluble enzymes* can be extracted by digesting the finely divided material which contains them with water, saline, or glycerol. The enzyme solution is then poured off, pressed out or separated by centrifugalisation, according to circumstances, and either used directly or

submitted to some process of purification. In some cases it is necessary or advisable to treat the material with dilute acid to convert the inactive proenzyme or zymogen of the cell into the active enzyme. As in the instances of invertase and maltase, it is often essential that the cell shall be killed before being submitted to extraction. This is best accomplished in those cases by treatment with chloroform or ether (invertase) or by drying and heating the yeast (maltase).

2. *Insoluble or endo-enzymes* are extracted by first of all rupturing the cells by some process of grinding, and then removing the liquid cell contents by simple pressure with or without the addition of some substance like kieselguhr, which greatly facilitates the process, but has the disadvantage of retaining some of the enzyme. A typical instance of this is afforded by the preparation of yeast juice from yeast by the method of E. and H. Buchner and Hahn, which is described below under the heading of *Alcoholic fermentation*. In other cases, the tissue or organ may be simply minced or frozen and finely sliced, and may then be extracted with water or saline.

Dry preparations of enzymes. A solution of an enzyme in an aqueous fluid often loses its characteristic properties very quickly, either on account of the instability of the enzyme itself, or because of the presence of other enzymes which bring about its decomposition. Such solutions are, moreover, extremely liable to infection by moulds, yeasts, and bacteria, and must either be kept at a low temperature or treated with some antiseptic. Dry preparations are found to be much more permanent, and, when quite dry, can be kept for long periods without undergoing much loss of power.

They may be obtained, in the first place, by the evaporation of the solution *in vacuô* at as low a temperature as possible, the product being usually a scaly mass. A second and often more convenient method consists in precipitation by alcohol, nearly all enzymes being insoluble in 70–90 p.c. alcohol. The chief practical difficulty of this method lies in the fact that aqueous alcohol frequently appears to exert an extremely detrimental effect on the enzyme, so that the process must in such cases be carried out with great rapidity. The final dehydration is usually effected by treatment of the precipitate with absolute alcohol and then with ether, a fine white powder being thus obtained.

It is not, however, in all cases necessary to extract the enzyme from the organism which contains it. Thus, for example, crushed castor-oil seeds are commonly used for the purpose of decomposing fats by means of the lipase which they contain. Buchner and his colleagues have, moreover, been able to effect several types of fermentation (alcoholic, lactic, acetic) by means of the cells of the organism, which have been simply killed by dry heat or killed and dehydrated by treatment with alcohol and ether or with acetone.

Purification of enzymes. The preparations obtained by the foregoing methods are all extremely crude, and contain, in addition to other enzymes, large proportions of extraneous matter, chiefly consisting of mineral salts, especially phosphates, proteins, and carbohydrates. Many attempts have been made to remove these by various processes of chemical precipitation (lead acetate, &c.), salting out, dialysis, treatment with yeast to remove sugars, &c., and thus to arrive at a pure enzyme. Some of these cases are mentioned later on, and there is no doubt that a considerable degree of purification can be effected by these methods. The usual experience has, however, been that with increasing freedom from such substances, the enzyme becomes more and more susceptible of change, and finally loses its activity before anything which can be regarded as an individual chemical compound has been isolated.

Mode of action of enzymes. Enzymes act as catalysts, but differ from catalysts of known symmetrical constitution in being specific in their action. The three disaccharides, sucrose, maltose, and lactose, for example, are all hydrolysed by the same acids, although at different rates, whereas each of them requires for its enzymic hydrolysis a special enzyme, which has no action whatever on the other two. The most probable view as to the mode of action of enzymes upon the substance to be decomposed, known as the *substrate* or *zymolyte*, is that in the first place some sort of combination between the two occurs, and that this is then followed by the comparatively slow breaking up of this complex, with liberation of the enzyme and the products of decomposition of the zymolyte. As soon as a certain limit of concentration of the substrate is reached, therefore, the limit of this rate of decomposition is attained, and any further increase in the concentration of the substitute is then unable to produce any increase in the number of decompositions per unit of time, or in other words, after a certain concentration is reached, equal amounts of the substrate will be decomposed in equal times. In presence of an excess of enzyme, on the other hand, the rate of action will vary with the concentration of the substrate. These conditions appear to be realisable in most cases of enzyme action, but since the absolute concentration of the enzyme is usually very small, decomposition of equal amounts in equal times is usually the more obvious.

Most of the enzymic decompositions which have been studied from this point of view are cases of hydrolysis, which, in the presence of acids alone follow the usual course for which the equation $K = 1/t(\log a/a-x)$ holds. This same expression often but not invariably holds for the enzymic reaction when excess of enzyme is present, at all events over a short range of concentration. When, however, the relations of concentration are such that equal amounts are decomposed in equal times, K, calculated by the foregoing expression, would increase with the time instead of being constant. On the other hand, anything which lessens the effective concentration of the enzyme will lower the rate of action and lead to a decrease of K. In many enzyme actions, there are at least three causes which tend to produce this effect. In the first place, the enzyme itself tends to become inactive. This change sometimes proceeds too slowly to have any effect on the result (*e.g.* in Senter's experiments on the decomposition of hydrogen peroxide by hæmase); in other cases, it occurs so rapidly as to influence the velocity very perceptibly (*e.g.*

in alcoholic fermentation by yeast juice, in which the fermentation ceases for this reason). In the second place, the products of the reaction often diminish the rate of change to a greater or less extent. Thirdly, a state of equilibrium is often attained short of complete decomposition, and this also causes a decrease in K. Very valuable information can be obtained about the course of the reaction by determining the *initial velocity* of the change under various conditions of concentration, as these inhibiting influences are thereby, to a large extent, eliminated. In this way, A. J. Brown showed that the apparent monomolecular course of the inversion of cane sugar by invertase was, in reality, due to secondary effects. When a series of concentrations of sugar were taken, the initial rates of change were found to be equal, whereas in presence of the products the rate of change diminished almost in agreement with the monomolecular law. This same effect is obvious in the results of Hudson with cane sugar, and of Kastle and Loovenhart with the decomposition of ethyl butyrate by lipase.

It appears, therefore, that, as a rule, the velocity curve of an enzyme reaction expresses the resultant of a very complicated system of phenomena, and can only be properly interpreted when a considerable number of experiments have been made to ascertain all the factors concerned.

When the substrate is present in large excess, increase of concentration of the enzyme frequently increases the rate of change proportionally, in agreement with the usual experience with inorganic catalysts. This is, for example, true for invertase. In some cases, however, the rate increases in proportion to a fractional power of the concentration of ferment. This is the case when pepsin acts on dissolved albumins, the amount of action in equal times being proportional to the square root of the concentration of pepsin (Schütz), and a similar rule appears to hold for many enzyme actions. It is explained by Arrhenius on the ground that the enzyme combines with the products of the reaction (Immunochemie, Leipzig, 1907). In other cases, the amount of action is found to be constant when the product of amount of ferment and time is constant, or $F \times t = k$. This holds for the action of pepsin on coagulated albumin, for that of trypsin on caseinogen (Hedin), and in many other cases.

The inhibiting influence of the products of the reaction is in many cases specific, numerous instances of this having been observed among the sugars and amino-acids. Thus invertase is inhibited by fructose (A. J. Brown), but not by glucose (Armstrong); lactase by galactose but neither by fructose nor glucose, &c.

As regards the nature of the combination between enzyme and substrate, very little is known. Many investigators, however, adopt the view of Bayliss that it is of the nature of adsorption between the particles of the colloidal enzyme and the substrate, and find in this an explanation of such relations as are exemplified by the proportionality between amount of action and the square root of the concentration of enzyme, discussed above. It is in favour of this view that enzymes are colloidal substances and that enzyme actions are therefore cases of catalysis in heterogeneous systems (*see* Bayliss, 1919, The Nature of Enzyme Action, vii.).

Whatever the nature of the combination, it appears to render the enzyme less susceptible of change whether by rise of temperature, spontaneous decomposition, or the action of other enzymes.

Conditions of enzyme action. The rate of action depends on several factors, in addition to the concentrations of enzyme and substrate.

Temperature.—The effect of temperature is primarily to raise the rate of reaction. The temperature coefficients of enzyme actions are, in general, of the same order as those of ordinary chemical changes (emulsin, amylase, rennin), but are sometimes considerably higher (trypsin), and in other cases lower (lipase, catalase). The fact that rise of temperature gradually inactivates the enzyme gives rise to the phenomenon of an *optimum temperature* above which rise of temperature causes a decrease in the measurable rate of the reaction. This optimum naturally varies with the duration and conditions of the experiment.

Hydrogen ion concentration $[H^{\cdot}]$. It has been shown by Sörensen (Biochem. Zeitsch. 1909, 21, 131, 201, 279; 22, 352) that this is a most important factor in enzyme action, affecting both the rate of reaction and the rate of inactivation of the enzyme. For each enzyme an optimum $[H^{\cdot}]$ exists, and according to Michaelis (Biochem. Zeitsch. 1909, 16, 81, 486; 17, 231; and many other papers), who regards the enzymes as amphoteric electrolytes, this is the $[H^{\cdot}]$ at which the greatest number of active molecules of enzyme exist, these being in some cases the anions (diastase, maltase, trypsin), in other the cations (pepsin), and in others the electrically neutral particles (invertase). In practice, Sörensen's 'buffer' solutions, such as mixtures of the mono- and di-hydrogen phosphates, can be used to regulate the $[H^{\cdot}]$ and thus ensure the optimum or any other required condition.

Inactivation of enzymes. All enzymes in aqueous solution become inactivated when the temperature is raised sufficiently, but the rate of inactivation varies for the different enzymes, and also depends very greatly on the $[H^{\cdot}]$ of the solution. It is usually very rapid at about 60°–70°, but in a few cases (some oxidases and proteases) the enzyme is not completely inactivated by boiling for a few minutes. The process of inactivation takes the course of a monomolecular reaction (peroxidase of milk), and the temperature coefficient of the change is in this case exceedingly high (2 for 1°, Zilva, Bio-Chem. J. 1914, 8, 656) and almost equal to that of the denaturation of albumin by heat (1·9, Chick and Martin). Enzymes are also inactivated at atmospheric temperatures by acids, and even more readily by alkalies.

Reversibility of enzyme action: synthetic action of enzymes. Since enzymes act as catalysts, it might be expected from analogy with catalysts of known composition that they would bring about conditions of equilibrium by affecting the velocities both of the reaction itself and of the reverse reaction (Tammann, Zeitsch. physiol. Chem. 1892, 16, 271). Thus it might be expected that an enzyme which effected the hydrolysis of a disaccharide into two hexose molecules would, when added to a mixture of these two hexoses in the proper concentration, synthesise the disaccharide. In each case the reaction would proceed until equilibrium was produced, and the same equilibrium would be attained whether the disaccharide or the mixed hexoses formed the starting-point.

This extremely important property of enzymes was first experimentally demonstrated by Croft Hill (Chem. Soc. Trans. 1898, 634) in the case of the action of maltase on maltose, and so many instances have since been observed that reversibility of action may now almost be taken as a general property of enzymes.

The simplest case, so far observed, is the action of lipase on esters of the fatty acids which exhibits all the characteristic features of a reversible reaction (Kastle and Loevenhart, Amer. Chem. J. 1900, 24, 491). These observers found that the hydrolysis of ethyl butyrate by the lipase of the pancreas or liver of the pig was always incomplete, and that when this enzyme was added to a mixture of butyric acid and alcohol (N/30), about 5 p.c. of the butyric acid was converted into ethyl butyrate in 40 hours at 25°, no ester being formed in a control experiment with the boiled enzyme solution.

The reaction studied by Croft Hill deserves consideration as the first observed case of synthesis resulting from enzyme action. The change in question was subsequently found to be of great complexity, and unanimity of opinion on the question has not yet been attained. The essential facts observed by Hill were: (1) that when concentrated glucose solution was acted on by the maltase of yeast, a portion of the glucose was converted into a disaccharide of higher rotation and lower reducing power; (2) that when such a solution was diluted, the disaccharide was reconverted almost completely into glucose. These observations were interpreted to mean that in concentrated solution, a certain proportion of maltose (15 p.c. of the glucose in a 45 p.c. solution) had been formed synthetically from the glucose, and that on dilution the condition of equilibrium had been shifted in the direction of almost complete decomposition of the maltose back again into glucose. It was, however, subsequently found by Emmerling (Ber. 1901, 34, 600), that the disaccharide formed consisted chiefly of a sugar isomeric with maltose, which was identified by Emmerling as the *iso*maltose obtained by Fischer by the action of acids on glucose, but was regarded by Croft Hill as a new sugar, revertose. E. F. Armstrong (Proc. Roy. Soc. B, 1905, 76, 592) confirmed Emmerling's result as to the nature of the chief product formed, and further obtained the paradoxical result that emulsin which decomposes *iso*maltose, but not maltose, converts glucose into maltose, and not, as might have been expected, into *iso*maltose. Each enzyme, therefore, according to Armstrong, produces from glucose the disaccharide which it is unable to hydrolyse.

This remarkable result has not yet been confirmed, and Armstrong did not ascertain whether the maltose formed by the action of emulsin was decomposed by the same enzyme preparation when its solution was diluted. Moreover, only a very small proportion of maltose appears to have been formed. The simplest explanation of Croft Hill's experiment seems, therefore, to be that adopted by Bayliss, that the maltase employed contained emulsin (which has since that time been shown by Henry and Auld (Proc. Roy. Soc. 1905, B, 76, 568) to be present in yeast), and that each enzyme synthesised from glucose the particular disaccharide which it was capable of decomposing (*see also* E. F. Armstrong, The Simple Carbohydrates and Glucosides, 75; Fajans, Zeitsch. physikal. Chem. 1910, 73, 25; 75, 232).

A suggestion has also been advanced that the synthesis and hydrolysis of the same compound are effected by different enzymes which occur together but are each only able to discharge the single function of hydrolysis or synthesis (*see* Rosenthaler, Biochem. Zeitsch. 1908, 14, 238; 1909, 17, 257). This idea is rendered improbable by the fact that in many cases the same state of equilibrium is attained when enzymes of different origin are employed, and is moreover inconsistent with the conception of an enzyme as a catalyst (Bayliss).

It has, however, been pointed out by Fajans (*l.c.*) that the enzyme itself probably takes part in the equilibrium, and that therefore alteration in its concentration might affect the state of equilibrium. This fact would also explain the observation that the equilibrium in certain cases of decomposition of acid esters is not the same when attained by the use of enzyme as when brought about by acid. The practical conditions necessary for the demonstration of synthetic enzyme action are well exemplified in the work of Bourquelot (numerous papers in Compt. rend. since 1912), who has prepared a large number of glucosides from their products of hydrolysis by the action of emulsin. For this purpose he has found that the essential condition is the limitation of the amount of water present. Thus a solution of glucose in 85 p.c. alcohol is partially converted by emulsin into β-ethylglucoside, whereas this compound in aqueous solution is almost completely hydrolysed by the same enzyme. The synthetic action of enzymes is of enormous importance in the biological chemistry of the living organism, since it is probably by the aid of reactions of this kind that the whole work of building up the tissues is effected.

Asymmetric and selective action of enzymes. It has been shown by the researches of Marckwald, McKenzie, and others (Ber. 1904, 37, 349, 1368, 4696; Chem. Soc. Trans. 1905, 1373; 1906, 688) that in a reaction in which an asymmetric carbon atom is produced, the two possible optically active isomerides may be produced in unequal quantities provided that the possibility is afforded by the introduction of an optically active radicle that the resulting compounds shall not be optical antipodes. Thus the reduction of pyroracemic acid

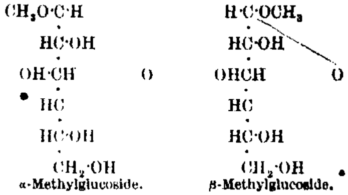
$$CH_3{\cdot}CO{\cdot}COOH$$

leads to the formation of inactive *dl*-lactic acid $CH_3{\cdot}CH(OH){\cdot}COOH$, whilst the reduction of menthyl pyroracemate $CH_3{\cdot}CO{\cdot}COOC_{10}H_{19}$ proceeds asymmetrically and yields an excess of the ester of the *l*-acid. More recently, it has been shown by Bredig and Fajans (Ber. 1908, 41, 752) that a catalytic reaction may proceed asymmetrically when the catalyst is itself optically active. This has been found to be the case when *l*-nicotine is employed to catalyse the decomposition of *dl*-camphorcarboxylic acid, the *d*-acid being in this case the more rapidly decomposed. This is precisely analogous to what occurs in many enzyme reactions, the asymmetric catalyst being in these cases the particular enzyme involved. There is, it is true, no direct positive evidence that enzymes are optically active substances, since, as already mentioned, no enzyme has as yet been isolated, but there is a strong probability that this is the case.

A good example of this asymmetric enzyme action is to be found in the work of Dakin (J. Physiol. 1904, 30, 253), who showed that the two optically active components of inactive *dl*-mandelic ester, which are hydrolysed at equal rates by alkalis, are decomposed at different rates by the fat-splitting enzyme or lipase of the liver, the dextro- ester being the more rapidly hydrolysed, so that after the removal of the resulting acid, the residual ester is lævorotatory. This action is probably to be explained by the formation of compounds between the enzyme and each of the components of *dl*-mandelic ester. The enzyme being, as explained above, itself an optically active substance, two different compounds are formed and these are decomposed at different rates. Many instances of this asymmetry of action are known among the chemical changes produced by micro-organisms. Thus the oxidation of inactive hydroxy acids (McKenzie and Harden, Chem. Soc. Trans. 1903, 83, 424), and of the amino acids by moulds, which was used by Pasteur for the resolution of such compounds, proceeds in a precisely similar manner; both of the components are attacked, but one more rapidly than the other. Similarly, the so-called alcoholic fermentation of the amino acids by yeast, as the result of which they are converted into carbon dioxide, ammonia, and an alcohol, takes place more rapidly with one of the components than with the other, so that by this means *l*-alanine and *d*-leucine can readily be prepared from the inactive synthetic acids (Ehrlich, Biochem. Zeitsch. 1906, 1, 8), the other component being, in each case, more easily decomposed.

An extreme case of this asymmetry of action is presented by many enzymes which only act on one stereoisomeride, and leave the other entirely untouched. Some remarkable instances of this kind have been revealed by the researches of Fischer and his colleagues on the enzymes which bring about the hydrolysis of the disaccharides and the glucosides. The relations between enzyme and zymolyte, which exist in this group of compounds, have been likened by Fischer to those which exist between a lock and key. The enzyme is capable of combining with one stereoisomeride, but is of such a structure that not only does the change to the opposite optical isomeride prevent combination, but even a change in the arrangement of the groups which condition asymmetry round a single carbon atom in the molecule of the sugar, just as the change of a single ward of a lock prevents the key from fitting it. The classical example of this relation is afforded by the behaviour of maltase on the one hand, and emulsin on the other, to the various disaccharides and glucosides.

Glucose forms two stereoisomeric methyl esters, which only differ from one another in the arrangement of the groups round the terminal carbon atom, so that their configurations may be represented as follows :—



α-Methylglucoside. β-Methylglucoside.

One of these is arbitrarily known as α-methylglucoside, and the other as β-methylglucoside. Of these, the α- compound only is attacked by maltase and the β- compound only by emulsin, and precisely similar relations exist between the α- and β-ethyl glucosides. Hence maltase has received the more precise name of α-glucosidase (or sometimes α-glucase), whilst emulsin (or that constituent of the complex usually termed emulsin, which effects this particular change) is termed β-glucosidase. Neither of these enzymes will attack the β- and α-methyl glucosides of *l*-glucose, which are the exact optical antipodes or 'mirror images' of the α- and β-methyl *d*-glucosides, and moreover they also have no action on the corresponding derivatives of *d*-mannose, *d*-galactose, and *l*-xylose, although in each of these three cases the difference between the unattacked compound and the corresponding glucose derivative extends only to one carbon atom. On the other hand, β-methyl tetramethylglucoside, in which four of the hydrogens of the hydroxyl- groups of β-methyl glucoside have been replaced by methyl, is hydrolysed by emulsin, so that this extensive introduction of the methyl- group has less effect than a change in the symmetry of a single carbon atom.

The other enzymes capable of hydrolysing disaccharides are equally specific. Invertase, for example, hydrolyses cane sugar (and possibly raffinose, which, like cane sugar, contains the fructose group), but has no action on maltose, lactose, or the α- and β-methyl glucosides. Similarly, lactase only attacks lactose, and not cane sugar, &c.

The alcoholic enzyme of yeast also possesses a highly specific character, but is not affected by such small changes in configuration as are maltase and emulsin. Thus *d*-glucose, *d*-mannose, and *d*-fructose are all fermentable by yeast, whilst, on the other hand, *l*-glucose, *l*-mannose, and *l*-fructose are not fermentable, and this is also true of the pentoses.

Similar results have been obtained by Fischer and Abderhalden (Zeitsch. physiol. Chem. 1905, 46, 52) in examining the action of pancreatic juice on the synthetic polypeptides. Only one half of the inactive compound is attacked and the products of hydrolysis are always those active amino-acids which are contained in the natural proteins. Thus *dl*-alanylglycine

$$CH_3{\cdot}CH(NH_2){\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}COOH$$

yielded glycine and *d*-alanine as hydrolysis products, *l*-alanylglycine being left untouched, All those facts afford the strongest evidence that combination between enzyme and zymolyte precedes the decomposition of the latter, and there is little doubt that similar conditions hold generally for the synthetic action of enzymes, although but few instances of this have hitherto been studied. A striking case in point is the combination between hydrocyanic acid and benzaldehyde. Ordinarily these substances combine to form inactive benzaldehyde cyanohydrin $C_6H_5\cdot CH(OH)\cdot CN$. When, however, this reaction is carried out in the presence of emulsin (or rather of that constituent of emulsin which is distinguished as hydroxynitrilase), the resulting product is optically active, a greater proportion of the *d*- than of the *l*-cyanohydrin having been formed (Rosenthaler, Biochem. Zeitsch. 1908, 14, 238), and in one case the *d*- compound being the sole product.

In nature, the asymmetry of action of synthetic enzymes is of the most far-reaching importance, as is evidenced by such facts as that the sugars, proteins, and many other naturally occurring compounds, are all optically active. Moreover, the asymmetry of action is so great that in many cases, *e.g* the sugars, the optical antipodes of the compounds appear not to occur at all.

Zymogens. The formation of enzymes in the cell is a subject of great importance, about which very little is known. In many cases, however, it has been ascertained that the cell contains an inactive substance, termed a zymogen or proferment, which subsequently becomes active and can often be rendered so by treatment with dilute acid. A very striking instance is afforded by the inactive trypsinogen of the pancreas. This substance is contained in pancreatic juice, and is quite inactive. When it is mixed with intestinal juice it is converted into active trypsin, by the action of a specific substance known as *enterokinase*, which is itself in all probability an enzyme. A case of even greater complexity is that of the enzyme thrombase, which brings about the clotting of blood.

Coenzymes. Some enzymes are incapable of producing their characteristic effects in the absence of a second substance, usually of a less complex character, which is therefore termed a coenzyme. The nature and functions of this class of substance are little understood (*see Alcoholic fermentation*).

Classification and nomenclature of enzymes. The nomenclature of enzymes is based on the principle that the name should indicate the substance acted upon by the enzyme, and should end with the syllable *-ase*, which is adopted as a specific termination, signifying an enzyme. This system introduces some difficulties, as certain compounds are decomposed in different ways by different enzymes (*e.g.* amygdalin and raffinose), and some enzymes decompose many different compounds (*e.g.* the digestive enzymes). These difficulties are avoided as far as possible by the use of special terms, such as emulsin, tryptase, invertase, lipase, and further specification is also sometimes attained by adding the names of the products formed.

Some confusion exists in actual practice, owing to the name, not of the substance decomposed, but of the product being prefixed to the termination -ase. Thus alcoholase is occasionally used for the alcohol-producing enzyme of yeast, but such terms should, as far as possible, be avoided, as well as those which simply denote the origin of the enzyme, such as hæmase (for the catalase of blood).

The simplest and most natural mode of classifying enzymes is by the nature of the reactions which they catalyse. Each group may then be further subdivided according to the nature of the compound upon which the specific action is exerted.

The chief enzymes at present known thus fall into the following groups, which agree in the main with those adopted by Oppenheimer, Euler, and other writers.

A. Enzymes producing hydrolysis (hydrolases).

1. Lipases, decomposing fats and esters; sometimes divided into:

(*a*) Esterases, decomposing simple esters.

(*b*) Lipases, decomposing fats and lipins (lipoid compounds), such as lecithin, &c.

2. Enzymes hydrolysing the nucleic acids and their primary products of hydrolysis (nucleases, &c.).

3. Enzymes hydrolysing the complex saccharides and glucosides (carbohydrases).

(*a*) Disaccharases, such as invertase, maltase, lactase, melibiase, &c.

(*b*) Tri- and tetra-saccharases, such as raffinase.

(*c*) Polysaccharases, such as diastase or amylase, inulase, cytase or cellulase, glycogenase, &c.

(*d*) Glucosidases, such as emulsin, rhamnase, &c.

4. The digestive enzymes, or proteases, hydrolysing the proteins, polypeptides, amides, and analogous compounds. This is a very complex group, the precise relations of which are not at all understood, there being at present no available information as to the number of enzymes concerned in such a process as peptic or tryptic digestion. A good deal of confusion exists in the nomenclature of these enzymes (*see* Fisher, Biochem. J. 1919, 13, 424)

(*a*) Simple amidases, causing the hydrolysis of various amino-compounds, such as urea, arginine, adenine, &c.

(*b*) Peptases and ereptases, decomposing polypeptides into amino-acids.

(*c*) Proteinases, which hydrolyse the albumins.

(i) Trypsin or tryptase, comprising a large number of enzymes, occurring both in animal and vegetable organisms, which decompose proteins and carry on the decomposition to the stage of polypeptides or possibly even to that of amino-acids.

(ii) Pepsin or pepsinase, comprising the enzymes of the animal stomach and of some plants, which in acid solution hydrolyse proteins, producing albumoses, peptone, and polypeptides.

B. Enzymes producing coagulation (coagulases).

1. Thrombase, which produces the clotting of blood.

2. Chymase, or rennet, which effects the curdling of milk.

3. Pectase, and similar enzymes.

C. Enzymes producing oxidation (oxidases and peroxidases).

1. Alcohol oxidases, oxidising alcohol to acetic acid.

2. Aldehydases, converting aldehydes into acids.

3. Purinoxidases, effecting the oxidation of the purine bases.

4. Phenolases, tyrosinases, &c., which effect the oxidation of many aromatic *p*-hydroxy- and amino- derivatives.

D. Enzymes producing reduction (reducases), or simultaneous reduction and oxidation.

E. Enzymes producing decompositions involving rupture of a carbon chain. These are sometimes known as zymases, or fermentation enzymes.

1. Enzymes of lactic acid fermentation.

2. Enzymes of alcoholic fermentation.

3. Many other enzymes doubtless fall into this group, since there is little doubt that the various fermentative changes brought about by bacteria, &c., are largely due to enzymes of this class.

F. Enzymes producing the decomposition of hydrogen peroxide into water and oxygen (catalases).

Any attempt at a detailed account of the enzymes is impossible on account of limitations of space, and only the best investigated can be even briefly described.

Enzymes producing Hydrolysis.

Lipase. Enzymes capable of hydrolysing fats, lecithins, and the alcohol esters of the fatty acids occur both in the animal and vegetable kingdoms. Some authorities distinguish between the ester-decomposing enzymes, which they term esterases, and the true fat-splitting enzymes or lipases, but it is doubtful whether our knowledge of the subject is sufficient to justify this. The difficulty of discrimination between different enzymes in this group is greatly increased by the facts that not only do the enzymes themselves appear to be insoluble in water, but the fats are also insoluble. These circumstances render the determination of the rate of action extremely uncertain.

The lipases of the animal body occur practically in all the tissues, but the action of most of these appears to be confined to the decomposition of esters, such as ethyl butyrate (*see* Kastle and Loevenhart, Amer. Chem. J. 1900, 24, 491; Porter, Biochem. J. 1916, 10, 523).

The chief fat-splitting enzymes of the body are found in the secretions of the pancreas and intestine. It seems probable that at all events the greater part of all absorbed fat is hydrolysed before absorption, and this process takes place in the intestine. These enzymes are extremely sensitive to acids and oxidising agents; they decompose alcohol esters as well as fats. The filtered extract and the residue prepared from these insoluble enzymes are both inactive, whereas the mixture is active, and the inactive residue can be rendered active by the salts contained in bile (Magnus, Zeitsch. physiol. Chem. 1904, 42, 169; 1906, 48, 373; Rosenheim, J. Physiol. Proc. Feb. 19, 1910, 14). How far this phenomenon depends upon the solubility relations of the enzyme or the fat, is not known.

The vegetable lipases occur in the form of zymogen in the seeds, and become active during germination. The enzyme of castor-oil seed has been the most thoroughly investigated. This seed is stated to contain an esterase, soluble in water, and a lipase, insoluble in water, which can be extracted by 1·5 N NaCl (Falk, J. Amer. Chem. Soc. 1912–15). The powder obtained by extracting the castor-oil bean with ether is almost inactive, but is rendered active by treatment with acid (N/10 sulphuric), and then acts most effectively when properly emulsified with the fat and a small proportion of acetic acid (Connstein, Hoyer, and Wartenberg, Ber. 1902, 35, 3988; Jalander, Biochem. Zeitsch. 1911, 36, 435; Kita, Chem. Soc. Abstr. 1918, i. 274, 1919, i. 503). Under favourable conditions it is so efficacious that it is employed technically for the hydrolysis of fats.

The synthetical action of animal lipase (or esterase) and its asymmetric decomposition of *dl*-esters have already been mentioned.

Invertase. Our knowledge of this enzyme, which brings about the hydrolysis of cane sugar to fructose and glucose, and owes its name to the inversion of the direction of rotation from dextro- to lævo-, which accompanies the change, is largely due to the classical researches of O'Sullivan and Tompson (Chem. Soc. Trans. 1890, 834). It occurs in many, but not all, species of yeast and in many moulds and bacteria, as well as in the higher plants and the intestine of animals. It is usually prepared from brewers' yeast; the enzyme can only be very imperfectly extracted from the living cells, especially when a young and vigorous culture is employed, but readily passes into solution in water when the yeast has been dried and heated or treated with chloroform, toluene, or alcohol. It is also present in the yeast-juice obtained by Buchner's grinding process, but is best prepared by allowing the pressed yeast to stand in a flask until it has become liquid, precipitating with 47 p.c. alcohol, and grinding the precipitate with absolute alcohol. Two kilos of yeast thus yield 5 grams of a grey powder containing about 3·5 p.c. of nitrogen and 5–8 p.c. of ash. The activity is usually expressed as the time taken for a solution of 0·05 gram of the material dissolved in 5 c.c. of 0·5 normal sodium dihydrogen phosphate to reduce the rotation of 20 c.c. of 20 p.c. cane sugar solution to zero at 20°, and for the preparation obtained as above, this is about 25 minutes. More active preparations can be obtained by redissolving in 25 parts of water, treating with 2·5 parts of animal charcoal for an hour, shaking with 10 parts of kaolin, and reprecipitating with alcohol. This process yields a material containing only 0·36 p.c. of nitrogen and 2·07 p.c. of ash, and having an activity of 14 minutes, this being the most active preparation so far described (Euler, Lindberg, and Melander, Zeitsch. physiol. Chem. 1910, 69, 152). This result, combined with earlier observations of Osborne (*ibid.* 1899, 28, 399) and Salkowski (*ibid.* 1901, 31, 306) render it improbable that invertase is a protein, but the question is by no means settled. In *Monilia candida* (Bon.), invertase occurs as a true endo-enzyme which can only be obtained from the cell by rupture of the membrane (Fischer and Lindner, Ber. 1895, 28, 3034; Buchner and Meisenheimer, Zeitsch. physiol. Chem. 40, 167). The action on cane sugar is accelerated by acids up to a certain concentration, the optimum concentration of hydrogen ions being $10^{-4·4}$ to $10^{-4·6}$ (Sörensen, Compt. rend. Carlsberg, 1909, 8, 1), and is at once inhibited by alkalis. The glucose is liberated in the α- form, so that the rotation falls when an alkali is added, and considerable errors may be introduced in estimations of the rate of action by polarimetric observations from this cause (O'Sullivan and Tompson; Hudson, J. Amer. Chem. Soc. 1908, 30, 1160). According to Visser (Zeitsch. physikal. Chem. 1905, 52, 257), equilibrium is attained in normal cane sugar solution in presence of invertase when 99 p.c. has been hydrolysed and a corresponding synthesis (1 p.c.) probably occurs in a solution of fructose and glucose, although this has not been directly proved

Solutions of invertase hydrolyse raffinose, a trisaccharide yielding fructose, glucose, and galactose on complete hydrolysis, but it is not certain whether this is actually due to the invertase or whether a specific raffinase is present. Certain organisms appear to hydrolyse cane sugar but not raffinose (*Mycoderma*) and others are stated to hydrolyse raffinose but not cane sugar (*Schyzosaccharomyces octosporus* (Bey.)). (For the use of invertase in the estimation of cane sugar, *see* J. Soc. Chem. Ind. 1911.)

Maltase is best obtained from well-washed bottom fermentation yeast by drying it *in vacuô*, powdering, heating gradually to 100°, and then digesting for 3 days at air temperature with 10 parts of 0·1 p.c. caustic soda solution and toluene, and finally filtering through a Chamberland filter into sterile flasks (Croft Hill, Chem. Soc. Trans. 1898, 634), a neutral or faintly acid solution being thus obtained. It can also be extracted directly with dilute ammonia from yeast killed by toluene (Willstätter). The enzyme cannot be prepared in an active state by precipitation with alcohol (Fischer, Ber. 1894, 27, 1113; Röhmann, *ibid.* 3251) although alcohol does not affect the maltase content of dry yeast or the dried extract. It rapidly hydrolyses maltose into glucose, 1 c.c. of the extract prepared as described above decomposing 20 p.c. of the maltose in 20 c.c. of a 2 p.c. solution at 30° in 40 minutes. The synthetic action of this extract has already been discussed. The action of the enzyme is at once destroyed by free alkali. Maltase is very widely distributed, occurring in many yeasts (but not in *S. Marxianus* (Hansen), *S. exiguus* (Hansen), *Saccharomycodes Ludwigii* (Hansen), *S. apiculatus* (Rees), and the lactose-fermenting yeasts), in many bacteria and moulds, in the foliage leaves and other parts of plants, and in germinated and ungerminated cereals, being localised mainly in the aleurone layer of the endosperm (Davis, Biochem. J. 1916, 10, 31; Daish, Biochem. J. 1916, 10, 49, 56), and in the small intestine, liver, kidneys, blood, and other tissues of mammals. Maltase, as already mentioned, only hydrolyses α-glucosides, and is therefore sometimes called α-glucosidase or α-glucase. It does not affect *iso*maltose, which is a β-glucoside, or trehalose, which is, however, hydrolysed by a special enzyme, *trehalase*, which occurs in moulds, some yeasts, and in green malt. The enzyme is very readily inactivated by traces of acid or alkali, and has an optimum temperature of about 40°, being greatly restricted in action at 55°.

Lactase is the specific enzyme which hydrolyses lactose into glucose and galactose. It also hydrolyses the β-alkylgalactosides, but not the α- compounds, and is therefore a β-enzyme. Its rate of action is diminished by galactose, but by no other sugar, and it therefore appears to combine with this substance as well as with lactose. Lactase occurs in a few yeasts, from which it may be extracted by grinding with glass powder and treatment with water (Fischer, Ber. 1894, 27, 2991, 3481) or by Buchner's process, but is best prepared by extracting kefir grains with water. It also occurs in some bacteria (*B. bulgaricus* (Grigoroff), &c.), and moulds (*e.g. Allescheria gayoni* (Sacc. & Syd.)) and in the small intestine of carnivorous and omnivorous animals and of young herbivora (Plimmer, J. physiol. Chem. 1906, 35, 20). An enzyme which decomposes lactose also occurs in the 'emulsin' obtained from almonds (H. E. and E. F. Armstrong and Horton, Proc. Roy. Soc. 1908, B, 80, 321), which probably differs from yeast lactase. Lactase, like maltase, effects the synthesis of a disaccharide, *iso*lactose (Fischer and Armstrong, Ber. 1902, 35, 3144).

Amylase or diastase. Enzymes capable of acting on starch with the production of a sugar appear to occur in nearly all living organisms. The whole question of the nature of these enzymes and of their action on starch is one of great complexity. The constitution of starch and of the dextrins formed from it being still unknown, no clear idea of the chemical action involved has been obtained, nor has any satisfactory criterion been found by which to judge whether only one or several enzymes are present. It is therefore impossible to do more in this place than give a very brief statement of the chief facts which have been ascertained. More complete information will be found in the article on BREWING, and in The Principles and Practice of Brewing, by Sykes and Ling (London, 1907).

The vegetable amylases or diastases are found in the germinating seeds and also in the leaves and other parts of the plant. The sources of the enzymes which have been chiefly investigated are malt and the mould *Aspergillus oryzæ* (Ahlburg Cohn), the amylase of which is known as takadiastase. The enzyme is extracted from malt by treatment with water or dilute alcohol, and may be several times precipitated by alcohol and further purified by dialysis (Lintner), or by being salted out from aqueous solution by ammonium sulphate (Wroblewski). The greatest degree of purification appears to have been attained by Fraenkel and Hamburg (Hofm. Beitr. 1906, 8, 389), by adding a suitable amount of basic lead acetate, filtering, fermenting with yeast, and drying. This preparation was strongly active, and showed none of the albumin reactions except a very faint Millon's reaction. It appeared to contain two enzymes, one non-diffusible and the other diffusible. On the other hand, Wroblewski's purest diastase had all the properties of an albumose.

Malt amylase is most active at a hydrogen ion concentration corresponding to $P_H=4·4–4·5$, that from *A. oryzæ* at $P_H=4·8$ (Sherman and colleagues, J. Amer. Chem. Soc. 1919, 41, 231).

Starch paste is first liquefied by malt extract, and the starch is then rapidly converted at 50° into a mixture of maltose and dextrins, about

81 p.c. of the starch being converted into maltose, and 19 p.c. into dextrin. The further conversion of this dextrin into maltose proceeds extremely slowly (Brown, Heron, Morris); but according to Maquenne and Roux, who have been confirmed by Bayliss, this 'stage' is due to insufficient activity of the enzyme, the conversion proceeding to completion when the enzyme is activated by the addition of a trace of acid. It appears to be undoubted that many complex dextrins intervene between starch and maltose, but their constitution is still unknown. The existence among the products of an *iso*maltose $C_{12}H_{22}O_{11}$ (Lintner), has been disproved (Ling and Baker). The action of diastase solution which has been heated to 68°–70°, is modified, so that less maltose and more dextrin are produced and more dextrin remains unchanged, whilst a certain proportion of glucose appears. This change in the mode of action of the enzyme may be due to an actual modification of the enzyme (Ling and Davis), but is regarded by many as evidence in favour of the theory (Wijsman, Beyerinck, Pottevin, Fraenkel, and Hamburg) that at least two enzymes are present, one of which (amylase) produces dextrin and the other (dextrinase) converts this into maltose. The separation of the enzyme into two parts by dialysis, one of which liquefies starch paste, and the other hydrolyses soluble starch, is also in favour of the existence of two enzymes. A different interpretation of the facts is due to Maquenne and Roux, according to whom starch contains two substances, *amylopectin*, to which the formation of the characteristic paste is due, and *amylose*, which is soluble. The amylose is converted by one enzyme of the diastase into maltose, whilst the amylopectin yields the dextrins under the action of a second enzyme. In mammals, diastatic enzymes are secreted by the salivary glands (ptyalin), the pancreas, and the intestine, and are also present in the liver, blood, muscular tissues, and most of the organs of the body. These enzymes convert starch and glycogen into maltose, but in many cases this is further changed into glucose by the maltase also present. The optimum activity of pancreatic amylase is exerted at $P_H=7$ (Sherman).

When a solution of pancreatic amylase is dialysed it becomes inactive both towards starch (Bierry, Gaja, and Henri, Soc. Biol. 1906, 60, 479) and glycogen (Norris, Biochem. J. 1913, 7, 622), the activity being restored by the addition of certain salts, more especially those of the halogen acids, whereas sulphates are inactive.

Emulsin. This name was originally applied by Liebig and Wöhler to the enzyme contained in almonds, which brought about the hydrolysis of amygdalin into hydrocyanic acid, benzaldehyde, and glucose. Further investigations (H. E. and E. F. Armstrong and Horton, Proc. Roy. Soc. 1908, B, 80, 321; Rosenthaler, Biochem. Zeitsch. 1910, 28, 408) have shown that the 'emulsin' of these workers contains a large number of distinct enzymes, and that the hydrolysis of amygdalin is a very complex phenomenon. It is most probable that the complete decomposition of this compound involves at least three enzymes, each capable of bringing about one stage in the reaction. Amygdalin has probably the formula

$$C_6H_5{\cdot}CH(CN){\cdot}OC_6H_{10}O_4{\cdot}O{\cdot}C_6H_{11}O_5$$

the glucose molecule being combined with the benzaldehyde residue to form a β-glucoside and the terminal glucose group as an α-glucoside. The stages of the hydrolysis are probably:

(1) Hydrolysis by *amygdalase*, forming α-glucose and *l*-mandelonitrile-β-glucoside (prunasin)

$$C_6H_5{\cdot}CH(CN){\cdot}O{\cdot}C_6H_{10}O_4{\cdot}O{\cdot}C_6H_{11}O_5+H_2O$$
$$=C_6H_5{\cdot}CH(CN){\cdot}O{\cdot}C_6H_{11}O_5+C_6H_{12}O_6$$

(2) Hydrolysis of this compound by a β-*glucosidase* (prunase) into β-glucose and *d*-benzaldehydecyanohydrin

$$C_6H_5{\cdot}CH(CN){\cdot}O{\cdot}C_6H_{11}O_5+H_2O$$
$$=C_6H_5{\cdot}CH(OH){\cdot}CN+C_6H_{12}O_6$$

(3) Decomposition of the cyanohydrin by *δ-hydroxynitrilase* or *benzcyanase*

$$C_6H_5{\cdot}CH(OH){\cdot}CN=C_6H_5{\cdot}CHO+HCN$$

The crude emulsin also effects the synthesis of *d*-benzaldehydecyanohydrin from benzaldehyde and hydrocyanic acid; but Rosenthaler (Biochem. Zeitsch. 1908, 14, 238; 1909, 17, 257) does not regard this as a reversed action of the enzyme, but as due to a different enzyme, and claims to have separated the two.

Amygdalase is, at all events in some cases, present in yeast (Henry and Auld, Proc. Roy. Soc. 1905, B, 76, 568); and Emmerling (Ber. 1901, 34, 600, 2206, 3810) has observed the synthetic production of amygdalin from *l*-mandelonitrile-glucoside and glucose in presence of crude yeast maltase. Emulsin also contains a lactase, to which reference has already been made.

Crude emulsin occurs in sweet almonds, from which it is extracted by digestion with chloroform water, and can be precipitated by alcohol. It is also found in many moulds as well as in yeast. The β-glucosidase also occurs in many bacteria (Twort, Proc. Roy. Soc. 1907, B, 79).

The β-glucosidase of emulsin hydrolyses the β-alkyl-glucosides and many of the natural glucosides, such as arbutin, salicin, prulaurasin, æsculin, and many others. It has been largely employed by Bourquelot for the biochemical synthesis of glucosides and disaccharides (*see* p. 134).

Other glucosidoclastic enzymes are myrosin, which hydrolyses the sinigrin of mustard, and tannase, which decomposes the natural tannins, and many more. Of considerable technical importance is the action of the enzyme contained in the leaf of the indigo plant, which is termed satase or indimulsin, and converts the indican of the leaf into glucose and indoxyl, the latter being then converted by oxidation into indigotin.

Many other specific glucoside enzymes are known (*see* The Simple Carbohydrates and Glucosides, by E. F. Armstrong, London, 1919).

The digestive enzymes or proteases comprise a great number of hydrolytic agents capable of replacing the $-NH_2$ group by $-OH$ (amidases or desamidases) or of causing the decomposition

$$R{\cdot}NH{\cdot}COR'+H_2O=R{\cdot}NH_2+R'{\cdot}COOH$$

to which the hydrolysis of the proteins appears to be mainly due. These are classed according to the completeness of the decomposition produced and the complexity of the compounds attacked under the various heads already given :

1. *Amidases or desamidases*, the most important of which accelerate the hydrolysis of urea and the conversion of adenine into hypoxanthine, and guanine into xanthine. Similar changes are often produced by micro-organisms (*see Alcoholic fermentation, Ammoniacal fermentation of urea*, and *Putrefaction*). A powerful urease occurs in many plants, especially in the seeds, one of the chief sources of the enzyme being the soya bean (*Glycine hispida*). It rapidly decomposes urea in dilute solution into ammonia and carbon dioxide, and, as its action is strictly specific (Armstrong and Horton, Proc. Roy. Soc. 1912, B, 85, 109), is employed for the estimation of urea in liquids (*e.g.* urine), which also contain other forms of combined nitrogen (Marshall, J. Biol. Chem. 1913, 14, 283; 15, 487, 495; Plimmer and Skelton, Biochem. J. 1914, 8, 70)

2. *Enzymes capable of hydrolysing various comparatively simple nitrogenous substances.* Among these are arginase (Kossel and Dakin, Zeitsch. physiol. Chem. 1904, 41, 321; 42, 181) and creatinase.

3. *Peptases or ereptases.* The synthetic production of the polypeptides by Fischer has rendered it possible to obtain a very large amount of information with respect to the nature and limitations of action of the proteoclastic enzymes, a line of research which has chiefly been followed by Fischer and Abderhalden (Lehrbuch physiol. Chem. Berlin, 1909). The relations appear to be very complex, and no approach to finality in the matter has yet been made.

In the blood, in all the organs and tissues, and in the intestinal juice are found enzymes which hydrolyse polypeptides, but are without action on the albumins. The relation to the polypeptides is highly specific, and only a very careful and thorough examination of the question will reveal how far the hydrolysis of various polypeptides is due to the action of different enzymes.

Of the synthetical polypeptides, only those which contain the naturally occurring optical isomerides of the amino-acids are decomposed.

Pancreatic trypsin itself decomposes many albumins down to the stage of polypeptides, and some of the latter are resolved into amino-acids, whereas others resist the further action of the enzyme, and are found in the digested liquid. It is, however, almost certain that pancreatic trypsin must be regarded as a complex consisting of a trypsin, capable of hydrolysing albumins down to the polypeptide stage, along with one or more peptases, which attack these simpler compounds (Schäffer and Terroine, J. Physiol. Path. 1910, 12, 884, 905; Wohlgemuth, Biochem. Zeitsch. 1912, 39, 302).

The decomposition of simple compounds, such as the dipeptides, alanyl-alanine, glycyl-glycine, and glycyl-tyrosine, provides an admirable opportunity for studying the kinetics of enzyme action.

4. *The Proteinases. Enzymes capable of hydrolysing the albumins.* (*a*) *Trypsin or tryptase.* This name belongs specifically to the enzyme secreted in the inactive (zymogen) form by the pancreas, as already described (p. 136), but is applied, as a general term, to a large number of enzymes, both of animal and vegetable origin, which attack albumins and produce from them polypeptides. Among the most important of these are the leucotryptase of the leucocytes of the blood, the autoclastic enzymes of animal tissues and organs, and the proteoclastic enzymes of the lower animals. In the vegetable kingdom, many similar enzymes occur, notably *papayotin* in the melon tree, *Carica papaya* (Linn.); *bromelin* in the pineapple, as well as the *endotryptases* of yeast, and many bacteria.

Pancreas trypsin is most active in presence of alkalis, the exact optimum concentration of hydrogen ions being different for different preparations and for different substrates (Long and Hull, J. Amer. Chem. Soc. 1917, 39, 1081), but being approximately 10^{-8} to 5×10^{-9} for fibrin and 3×10^{-6} to 5×10^{-7} for caseinogen; 0·2 p.c. of sodium carbonate is commonly employed. It also exerts a certain amount of action in very weak acid solution. The amount of hydrolysis is proportional to the amount of enzyme and the time of action, the concentration being indifferent (Löhlein, Hofm. Beitr. 1905, 7, 120; Hedin, J. Physiol. 1904, 32, 468; 1906, 34, 370).

Trypsin is readily taken up, probably by adsorption, by fibrin, and can thus be removed from solution. It is also adsorbed by animal charcoal and cannot be re-extracted from this substance by water (Hedin).

Substances which tend to inhibit the action of the enzyme and are termed antitrypsins, occur in blood serum, in parasitic worms, and in yeast, but the nature and function of these is as yet little understood (*see* Hedin, Zeitsch. physiol. Chem. 1907, 52, 412; Buchner and Haehn, Biochem. Zeitsch. 1910, 26, 171; Weinland, Zeitsch. Biol. 1902, 44, 1, 45).

(*b*) *Pepsin or pepsinase.* This enzyme is the characteristic digestive agent of the gastric juice of all vertebrates. It is secreted by the cells of the mucous membrane of the stomach in the form of an inactive zymogen, *propepsin*, which is converted into active pepsin by the hydrochloric acid of the gastric juice. It is also secreted by Brunner's glands in the intestine, and is stated to occur in a few flesh-eating plants, such as the various species of *Nepenthes* (pitcher plant), *Dionæa* and *Drosera* (sundew). The most characteristic properties of pepsin are that it only acts in acid solution, and that it does not hydrolyse any known polypeptide. It converts the albumins (phosphoproteins, nucleoproteins, gelatin, &c.) probably first into acid albumins and then into simpler compounds of unknown constitution. These were formerly classed as albumoses, precipitable by ammonium sulphate; and peptones, non-precipitable by this salt, but precipitable by phosphotungstic acid. The nature and individuality of the numerous compounds of these classes which have been described are still involved in obscurity, and all that can be said with certainty is that hydrolysis does not go so far as to produce simple amino-acids. The least impure form of pepsin appears to have been obtained by Pokelharing (Zeitsch. physiol. Chem. 1902, 35, 8), who simply dialysed the filtered gastric secretion of a dog, obtained by fistula, and

81 p.c. of the starch being converted into maltose, and 19 p.c. into dextrin. The further conversion of this dextrin into maltose proceeds extremely slowly (Brown, Heron, Morris); but according to Maquenne and Roux, who have been confirmed by Bayliss, this 'stage' is due to insufficient activity of the enzyme, the conversion proceeding to completion when the enzyme is activated by the addition of a trace of acid. It appears to be undoubted that many complex dextrins intervene between starch and maltose, but their constitution is still unknown. The existence among the products of an *iso*maltose $C_{12}H_{22}O_{11}$ (Lintner), has been disproved (Ling and Baker). The action of diastase solution which has been heated to 68°–70°, is modified, so that less maltose and more dextrin are produced and more dextrin remains unchanged, whilst a certain proportion of glucose appears. This change in the mode of action of the enzyme may be due to an actual modification of the enzyme (Ling and Davis), but is regarded by many as evidence in favour of the theory (Wijsman, Beyerinck, Pottevin, Fraenkel, and Hamburg) that at least two enzymes are present, one of which (amylase) produces dextrin and the other (dextrinase) converts this into maltose. The separation of the enzyme into two parts by dialysis, one of which liquefies starch paste, and the other hydrolyses soluble starch, is also in favour of the existence of two enzymes. A different interpretation of the facts is due to Maquenne and Roux, according to whom starch contains two substances, *amylopectin*, to which the formation of the characteristic paste is due, and *amylose*, which is soluble. The amylose is converted by one enzyme of the diastase into maltose, whilst the amylopectin yields the dextrins under the action of a second enzyme. In mammals, diastatic enzymes are secreted by the salivary glands (ptyalin), the pancreas, and the intestine, and are also present in the liver, blood, muscular tissues, and most of the organs of the body. These enzymes convert starch and glycogen into maltose, but in many cases this is further changed into glucose by the maltase also present. The optimum activity of pancreatic amylase is exerted at $P_H=7$ (Sherman).

When a solution of pancreatic amylase is dialysed it becomes inactive both towards starch (Bierry, Gaja, and Henri, Soc. Biol. 1906, 60, 479) and glycogen (Norris, Biochem. J. 1913, 7, 622), the activity being restored by the addition of certain salts, more especially those of the halogen acids, whereas sulphates are inactive.

Emulsin. This name was originally applied by Liebig and Wöhler to the enzyme contained in almonds, which brought about the hydrolysis of amygdalin into hydrocyanic acid, benzaldehyde, and glucose. Further investigations (H. E. and E. F. Armstrong and Horton, Proc. Roy. Soc. 1908, B, 80, 321; Rosenthaler, Biochem. Zeitsch. 1910, 28, 408) have shown that the 'emulsin' of these workers contains a large number of distinct enzymes, and that the hydrolysis of amygdalin is a very complex phenomenon. It is most probable that the complete decomposition of this compound involves at least three enzymes, each capable of bringing about one stage in the reaction. Amygdalin has probably the formula

$$C_6H_5{\cdot}CH(CN){\cdot}OC_6H_{10}O_4{\cdot}O{\cdot}C_6H_{11}O_5$$

the glucose molecule being combined with the benzaldehyde residue to form a β-glucoside and the terminal glucose group as an α-glucoside. The stages of the hydrolysis are probably:

(1) Hydrolysis by *amygdalase*, forming α-glucose and *l*-mandelonitrile-β-glucoside (prunasin)

$$C_6H_5{\cdot}CH(CN){\cdot}O{\cdot}C_6H_{10}O_4{\cdot}O{\cdot}C_6H_{11}O_5+H_2O$$
$$=C_6H_5{\cdot}CH(CN){\cdot}O{\cdot}C_6H_{11}O_5+C_6H_{12}O_6$$

(2) Hydrolysis of this compound by a *β-glucosidase* (prunase) into β-glucose and *d*-benzaldehydecyanohydrin

$$C_6H_5{\cdot}CH(CN){\cdot}O{\cdot}C_6H_{11}O_5+H_2O$$
$$=C_6H_5{\cdot}CH(OH){\cdot}CN+C_6H_{12}O_6$$

(3) Decomposition of the cyanohydrin by *δ-hydroxynitrilase* or *benzcyanase*

$$C_6H_5{\cdot}CH(OH){\cdot}CN=C_6H_5{\cdot}CHO+HCN$$

The crude emulsin also effects the synthesis of *d*-benzaldehydecyanohydrin from benzaldehyde and hydrocyanic acid; but Rosenthaler (Biochem. Zeitsch. 1908, 14, 238; 1909, 17, 257) does not regard this as a reversed action of the enzyme, but as due to a different enzyme, and claims to have separated the two.

Amygdalase is, at all events in some cases, present in yeast (Henry and Auld, Proc. Roy. Soc. 1905, B, 76, 568); and Emmerling (Ber. 1901, 34, 600, 2206, 3810) has observed the synthetic production of amygdalin from *l*-mandelonitrile-glucoside and glucose in presence of crude yeast maltase. Emulsin also contains a lactase, to which reference has already been made.

Crude emulsin occurs in sweet almonds, from which it is extracted by digestion with chloroform water, and can be precipitated by alcohol. It is also found in many moulds as well as in yeast. The β-glucosidase also occurs in many bacteria (Twort, Proc. Roy. Soc. 1907, B, 79).

The β-glucosidase of emulsin hydrolyses the β-alkyl-glucosides and many of the natural glucosides, such as arbutin, salicin, prulaurasin, æsculin, and many others. It has been largely employed by Bourquelot for the biochemical synthesis of glucosides and disaccharides (*see* p. 134).

Other glucosidoclastic enzymes are myrosin, which hydrolyses the sinigrin of mustard, and tannase, which decomposes the natural tannins, and many more. Of considerable technical importance is the action of the enzyme contained in the leaf of the indigo plant, which is termed satase or indimulsin, and converts the indican of the leaf into glucose and indoxyl, the latter being then converted by oxidation into indigotin.

Many other specific glucoside enzymes are known (*see* The Simple Carbohydrates and Glucosides, by E. F. Armstrong, London, 1919).

The digestive enzymes or proteases comprise a great number of hydrolytic agents capable of replacing the $-NH_2$ group by $-OH$ (amidases or desamidases) or of causing the decomposition

$$R{\cdot}NH{\cdot}COR'+H_2O=R{\cdot}NH_2+R'{\cdot}COOH$$

to which the hydrolysis of the proteins appears to be mainly due. These are classed according to

781, 1217). Bach (Ber. 1910, 43, 364) has, however, prepared active oxidases entirely free from manganese and iron, and it is probable that, when present, the salts of these metals only exert a secondary accelerating action on the oxidation process. The attempt of Willstätter and Stoll (Annalen, 1918, 416, 21) to isolate the enzyme from horse-radish resulted in a preparation having 3000 times the activity of the original material as measured by the production of purpurogallin from pyrogallol under standardised conditions. Chemically it appears to consist of a nitrogenous glucoside yielding a pentose and probably a hexose on hydrolysis. It contains 5·5 p.c. of ash, 0·46 of which is iron. The chief types of oxidising enzymes known are the following:

1. **The peroxidases**, which occur in all parts of plants. Their occurrence in animal tissues is difficult to establish, as blood produces all the reactions ascribed to peroxidases, and must therefore be absent before the presence of the latter can be proved (Batelli and Stern, Biochem. Zeitsch. 1908, 13, 44). A vigorous peroxidase occurs in milk.

2. **The enzymes producing coloured compounds** from **aromatic phenols,** &c. These may be known as phenolases. They produce the most varied oxidations, accompanied by colour changes, and according to Bach (Bach and Maryanovitsch, Biochem. Zeitsch. 1912, 42, 417) the enzymes obtained from various sources must be regarded as identical, since they all produce the same primary oxidising effects, although these are variously modified by the presence of salts, &c. The work of Bach and Chodat, discussed above, applies to these enzymes. According to Wheldale Onslow the browning of fruits on injury is due to the presence of a peroxidase and an aromatic compound containing the catechol grouping. The oxidation of the latter is effected by atmospheric oxygen, but is catalysed by a special enzyme (oxygenene), and results in the formation of a peroxide, the whole system then constituting an oxidase, and giving a blue colour with guaiacum (Biochem. J. 1919, 13, 1; 1920, 14, 535).

Laccase occurs in the juice of the lac tree of Tonkin (*Rhus vernicifera* (D.C.)), and brings about the oxidation of the yellow juice to the black lacquer (Yoshida, Chem. Soc. Trans. 1883, 43, 472; Bertrand, Compt. rend. vols. 118–122). It has also been found in many other phanerogams (lucerne, cabbage, potatoes, &c.) and in fungi. It accelerates the oxidation of *o*- and *p*-polyphenols (but not of *m*- compounds), and has no effect on tyrosine. Its solutions only lose their oxidising powers slowly when boiled.

Tyrosinase. Enzymes capable of oxidising tyrosine with production of coloured substances occur widely, both in the animal and vegetable kingdoms, frequently accompanied by laccase. According to Gortner (Chem. Soc. Trans. 1910, 110), both soluble and insoluble forms of tyrosinase occur in the meal worm (*Tenebro molitor*). The insoluble form contains iron, but no manganese, and is capable of oxidising a relatively large amount of tyrosine, producing a series of colour changes through pink, rose, violet, and blue-black to black (*melanin*). It also effects the oxidation of *p*-aminophenol, guaiacol, gum guaiacum, and 2 : 4-diaminophenol, but not of quinol or pyrogallol. Tyrosinase also occurs in many leaves, which become black on drying, and in bran. The blue colour observed when certain mushrooms are broken is not due to the action of this enzyme but to that of laccase (Bertrand). A very large number of *p*-hydroxyphenyl derivatives, as well as nearly all derivatives of tyrosine, tryptophan, and some of its derivatives, adrenaline, phenol, and *p*-cresol are oxidised.

Bach has shown (Biochem. Zeitsch. 1914, 60, 221) that the action of tyrosinase is very complex. Tyrosinase contains (1) an *amino-acidase*, which decomposes tyrosine with formation of some compound (probably *p*-hydroxyphenylacetaldehyde) which is capable of being acted on by an oxidase, or a peroxide and hydrogen peroxide:

$$OH{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH(NH_2){\cdot}COOH+H_2O$$
$$=OH{\cdot}C_6H_4{\cdot}CH_2{\cdot}CHO+NH_3+CO_2+[2H]$$

(2) A non-specific oxidase system (phenolase) capable of oxidising this product at the expense of atmospheric oxygen. In some cases the organic peroxide of this oxidase system is only present in traces, but the peroxidase is always abundant. The action of the aminoacidase only proceeds in the presence of a hydrogen acceptor, and this is produced from some substance present in the 'tyrosinase' by the action of atmospheric oxygen, so that the first stage of the change can only commence in presence of air.

When a mixture of tyrosine and tyrosinase is shaken in the air, oxidation commences, and a deep red coloured solution is formed. If the air be now replaced by nitrogen, this colour disappears, owing to reduction, and a colourless solution results. If this be boiled, the further action of the tyrosinase is prevented, but the liquid now gives all the colour changes characteristic of tyrosine when treated with hydrogen peroxide and a peroxidase (*e.g.* from horse-radish), although these have no action whatever on tyrosine itself.

The various oxidative fermentations brought about by micro-organisms are discussed later.

ENZYMES PRODUCING REDUCTION. REDUCASES.

Enzymes are also known in presence of which many compounds (colouring matters, aldehydes) are reduced. They occur very widely in animal tissues (liver, muscle), and in the higher plants, as well as in yeasts and bacteria. The source of the hydrogen in these reductions is water, and the change only proceeds in the presence of an oxidisable substance, which can act as an acceptor for the oxygen of this water. Hence these enzymes produce both reduction and oxidation simultaneously, and, as the process also involves the decomposition of water, it has been termed a hydroclastic oxido-reduction (Oppenheimer). According to Bach (Biochem. Zeitsch. 1911, 31, 443), whose views, however, require further experimental confirmation, the hydrogen forms an unstable perhydride of oxygen $H_2O{:}H_2$, which is decomposed in the presence of the enzyme, the hydrogen being passed on to the reducible substance. Hence he terms the enzyme a *perhydridase*, and regards the whole process as closely analogous to oxidation by means of a peroxide and a peroxidase.

On the other hand, Wieland and Thunberg (Stand. Arch. Physiol. 1920, 40, 1, where the literature is quoted) considered that the hydrogen is transferred directly from the oxidisable substance to the reducible substance by the enzyme, which is accordingly termed *dehydrogenase*.

Milk has long been known to contain an enzyme of this class (Schardinger's enzyme), which brings about the reduction of methylene blue in the presence of formaldehyde, but not in its absence, the aldehyde acting as oxygen acceptor. It has now been shown that the reducing enzymes of the tissues (Bach), and of yeast and some bacteria (Harden and Norris, Harden and Zilva), are of the same type. Dried yeast and zymin (p. 149), *Bacillus coli communis*, and rabbit muscle can be freed from the oxygen acceptor by washing, and then only reduce methylene blue in the presence of certain definite oxidisable substances, which, however, differ for the enzymes derived from different materials, so that these cannot be regarded as identical. The oxygen acceptor, in the case of the tissue reducases, is probably an aldehyde (Bach).

A special case of reducase action is the conversion of an aldehyde into an equimolecular mixture of the corresponding alcohol and acid (Cannizzaro's reaction), one molecule being reduced and a second acting as oxygen acceptor and being oxidised. This is brought about by an enzyme termed *aldehydase*, or better *aldehydomutase*, which occurs in the liver, lungs, and spleen (Parnas, Biochem. Zeitsch. 1910, 28, 274; Battelli and Stern, Biochem. Zeitsch. 1910, 29, 130). The oxidising effect of this enzyme on aldehydes, such as salicylaldehyde, had been known for some time (*see* Jacoby, Virchow's Arch. 1899, 157, 235; Zeitsch. physiol. Chem. 1900, 30, 135; 1901, 33, 128) before the simultaneous reducing action was observed.

Analogous to this enzyme, but distinct from it, is the *glyoxalase* of Dakin and Dudley (J. Biol. Chem. 1913, 14, 155, 423; 15, 463; 1914, 16, 505), which occurs in many animal tissues in the higher plants and in yeast, and converts glyoxal and its derivatives into the corresponding hydroxy-acids, oxidation and reduction occurring in the same molecule:

$$R\cdot CO\cdot CHO + H_2O = R\cdot CH(OH)\cdot COOH$$

It is strongly inhibited by pancreatic extract.

CATALASE.

This name was given by Loew (Bull. Agric. Washington, 1900) to the enzyme which has the power of catalysing the decomposition of hydrogen peroxide into water and oxygen. It has long been known that animal and vegetable tissues have the property of producing this decomposition, and, at one time, this was thought to be a general characteristic of all enzymes (Schönbein, J. pr. Chem. 1863, 89, 334). Further investigation, however, showed that this was not the case, but that this property belonged to a special, very widely distributed enzyme (Loew). The power of decomposing hydrogen peroxide is possessed by all the tissues of the animal body, and is most marked in the liver. Thus it was found by Batelli and Stern (Arch. Fisiolog. 1905, 2, 471) that 0·1 gram of guinea-pig liver evolved 5800 c.c. of oxygen from 1 p.c. hydrogen peroxide at 37°, whilst the corresponding number for the blood was 490 c.c., and for the muscle 34 c.c. The enzyme can be concentrated by extracting the tissue with water, precipitating with alcohol, extracting this with water, and again precipitating with alcohol. A similar process applied to blood yielded a clear faintly yellow solution of the enzyme, free from blood and from iron (Senter, Zeitsch. physikal. Chem. 1903, 44, 257; 1905, 51, 673). Preparations can be obtained from many plant tissues in a similar manner, as well as from yeast and many fungi and bacteria. It is not certain whether the enzymes derived from these various sources are identical, but Loew has distinguished the soluble and insoluble forms of the enzyme obtained by him from tobacco as β- and α-catalase, and Senter has named the enzyme from blood hæmase.

The catalytic function of the enzyme appears to be strictly limited to the decomposition of hydrogen peroxide. The oxygen is liberated in the gaseous state, and does not effect any oxidations other than can be brought about by free oxygen. The enzyme is very sensitive to the presence of free hydrogen ions, and, according to Sörensen, acts best in neutral solution, whilst alkalis and many salts exert an inhibiting effect. Hydrocyanic acid is a powerful inhibitant, but does not cause any permanent change in the enzyme. Hydrogen peroxide itself exerts a destructive action on the enzyme, and hence accurate measurements of the rate or amount of decomposition can only be made in dilute solution and in presence of a relatively large amount of enzyme. Under these conditions, the decomposition is monomolecular, and the velocity is proportional to the concentration of enzyme and of hydrogen peroxide, whilst with increasing concentration of hydrogen peroxide the velocity becomes relatively slower (Senter). As the oxygen appears to be produced in the molecular form, it is probable that the decomposition occurs in stages, either an intermediate compound of enzyme and hydrogen peroxide being formed which then breaks down, or a compound of the enzyme and oxygen which then reacts with a second molecule of the peroxide.

The reaction is analogous in many respects to the decomposition of hydrogen peroxide by colloidal platinum (Bredig). The catalase is, however, more efficacious, a solution of 0·001 gram per litre of catalase-containing material from blood having the same effect as a solution of colloidal platinum containing 0·006 gram (Euler, Hofm. Beitr. 1906, 7, 1).

The action of catalase is measured either by titration of the hydrogen peroxide present at various stages of the reaction or by direct measurement of the oxygen evolved. Estimations of the rate or extent of decomposition of hydrogen peroxide by the catalase of milk or of malt (van Laer) have been used in the analytical examination of these materials. A solution of vegetable catalase is used to remove the excess of hydrogen peroxide from cream which has been sterilised by the addition of this substance (Budde).

The physiological function of catalase in the animal body is not definitely known, but it is conjectured that it may be to decompose hydrogen peroxide or complex peroxides formed during processes of oxidation.

THE COAGULASES.

A number of enzymes exist which have the property of bringing about changes in various liquids which result in the formation of an insoluble material. The most important of these are:

(1) The production of a curd in milk by the enzyme of rennet (chymase).

(2) The coagulation of the blood by the enzyme thrombase.

(3) The coagulation of muscle.

(4) The formation of insoluble substances from the pectins of plants (pectase).

Most of these changes are exceedingly complicated, the coagulation of the blood being one of the most complex phenomena in the whole range of physiological chemistry. The only one which can be treated here is the action of rennet on milk.

Rennet, Rennin, or Chymase. Enzymes possessing the power of coagulating milk occur in the form of zymogen in the mucous membrane of the stomach of many animals, and are secreted into the gastric juice; similar substances are also found in many plants. Milk is also curdled by pancreatic trypsin Rennet is usually prepared by digesting the membrane of the stomach of the calf with 0·1–0·2 p.c. hydrochloric acid, or with glycerol or salicylic acid, and can be precipitated by alcohol. Some doubt exists as to the relation of rennet to pepsin, which is also secreted by the cells of the mucous membrane of the stomach. According to Pavlov (Zeitsch. physiol. Chem. 1904, 42, 415), the coagulation of milk is an effect of the action of pepsin under special conditions, whereas Hammarsten strongly supported the view that the two enzymes are distinct (Maly's Jahresb. 1872, 1874, 1877). The question is a very complex one, owing to the existence of anti-peptic and anti-rennet substances in the stomach extracts, but the balance of opinion now inclines to the belief that two independent enzymes exist.

Rennet converts the caseinogen of milk into casein, the change most probably (but not certainly) consisting in the hydrolytic decomposition of the molecule of caseinogen with production of casein and some other product. The casein thus produced is precipitated by calcium salts as an insoluble curd, and it is the formation of this precipitate which is observed in the curdling of milk by rennet. Solutions of caseinogen in the minimum amount of lime water or in caustic soda solution are not curdled by rennet, but after treatment give a precipitate with calcium salts.

The time required for curdling is proportional both to the concentration of enzyme and of caseinogen. The action is favoured by slight acidity and hindered by alkalinity. The optimum temperature is 37°–45° and the temperature coefficient of the reaction is about 3 for 10°. When the milk is boiled before being treated, the formation of curd is interfered with, probably owing to changes produced in the calcium salts of the milk. The enzyme is capable of curdling at least 1,000,000 times its weight of milk.

ALCOHOLIC FERMENTATION.

The production of carbon dioxide and alcohol from sugar is by far the most important of all technical processes of fermentation, and has, therefore, been more thoroughly investigated than any other change produced by micro-organisms. Although both alcohol and carbon dioxide are produced from sugar by many micro-organisms belonging to the class of bacteria, the power of bringing about the typical alcoholic fermentation, of decomposing sugar almost quantitatively into these two substances, is possessed among micro-organisms only by certain moulds, and by a group of unicellular fungi which belong to several closely allied families and are commonly grouped together as yeasts. The biology and mode of culture of these are treated in the article on BREWING.

Composition of yeast. The cell consists of membrane, cytoplasm, and nucleus, but much doubt exists as to the exact form of the nucleus and the changes which it undergoes during fermentation, budding, and spore formation. In the cytoplasm occur vacuoles, and at various stages in the life of the cell granules of chromatin and volutin are formed as well as fat droplets and glycogen.

Yeast, which has been pressed at about a half-ton per square inch, forms a friable, almost white mass, containing about 70 p.c. of water and alcohol, and 30 p.c. of solids. The composition of the dry matter of yeast varies so greatly with conditions of growth, &c., that no general statement is of much value. The ash, which amounts to 5–10 p.c. of the dry residue, consists essentially of potash (K_2O, 28–39 p.c.), magnesia (MgO, 4–6 p.c.), lime (CaO, 1–7 p.c.), and phosphoric oxide (P_2O_5, 45–59 p.c.), together with smaller quantities of sulphur trioxide, iron, silica, and traces of chlorine. The exact nature of the cell membrane is as yet undecided, but it appears to be closely allied to cellulose, although true cellulose is absent. The cytoplasm contains a coagulable albumin, a nuclein, glycogen, yeast gum, and a large number of other compounds, in part derived from these by hydrolysis.

General phenomena of alcoholic fermentation. 1. *The fermentable substances.* All yeasts which ferment glucose also ferment mannose and lævulose. The case of galactose is different, as some yeasts appear to ferment it imperfectly, and others not at all. It has been found by many observers and may now be regarded as established, that certain yeasts which do not normally ferment galactose readily acquire this property when they are cultivated in the presence of this sugar, as for example in hydrolysed lactose. Examples of this are *S. carlsbergensis* (H.), *S. cerevisiæ* (H.), *S. thermantitonum* (Johnson), &c. Indeed, according to Lindner, all the culture yeasts exhibit this property (*see* Slator, Chem. Soc. Trans. 1908, 217; Lindner, Wochensch. Brauerei, 1911, 28, 61).

The higher saccharides are not directly fermentable by yeast, but must first undergo hydrolysis to the simple hexoses. This is effected by hydrolytic enzymes present in the yeast, which can, as a rule, be extracted from the cell by appropriate methods. The ordinary culture yeasts employed in brewing, &c., contain maltase and invertase, but not lactase, and are therefore able to ferment maltose and cane sugar, but not lactose. Bottom yeasts appear invariably to contain melibiase, which decomposes melibiose into glucose and galactose, whilst this enzyme is lacking in top yeast. An analytical method for detecting bottom yeast in top yeast has been founded on this fact. In addition to this, practically all culture yeasts are able partially to ferment raffinose, which on hydrolysis yields melibiose and fructose, and they probably contain a special enzyme, *raffinase*, which produces this hydrolysis, although it is possible that this is due to the invertase. In the case of top yeasts, only the fructose thus produced undergoes alcoholic fermentation, the melibiose remaining unaltered, whereas the bottom yeasts decompose this also. Dextrin is also more or less slowly fermented by yeast, the hydrolysis being effected by a dextrinase or amylase. This property is of great importance in brewing, as a yeast which possesses a comparatively large amount of this enzyme is able to attenuate the wort to a greater extent, and to produce a larger yield of alcohol. Starch and glycogen are unaffected by yeast, probably because, owing to their highly colloidal nature, they are unable to penetrate the cell. Species of yeast are now known which are lacking in one or other of all these hydrolytic enzymes, and hence are incapable of fermenting the corresponding sugar. These have frequently been employed for the isolation of such a sugar as maltose from mixtures containing glucose or fructose, and for the analytical estimation of mixtures of sugars (Davis and Daish, J. Agric. Sci. 1913, 5, 437), and in fact their relations to the disaccharides are employed as a means of classification. Thus *S. marxianus* (H.) and *S. exiguus* (H.) ferment cane sugar, but not maltose; *S. rouxi* (Boutroux) ferments maltose, but not cane sugar; *S. fragilis* (Jörg), found in kefir, ferments lactose, and *S. mali* (Duclaux) only ferments the simple sugars and is without action on the disaccharides. No yeast appears to be able to ferment the synthetical disaccharides, such as *iso*maltose or glucosidogalactose, and this disability extends to the isomerides of the hexoses, such as sorbose, tagatose, &c., to the optical antipodes of the fermentable sugars which have been obtained by synthesis, and to the pentoses and tetroses. Beyond the simple sugars mentioned above, no other substance appears to be directly fermentable by yeast to alcohol and carbon dioxide, with the exceptions of a synthetical 9-carbon atom sugar and of glyceraldehyde and dihydroxyacetone, which, according to Bertrand, Buchner, and Meisenheimer (Ann. Chim. Phys. 1904, [8] 3, 181; Ber. 1910, 43, 1773), and Lebedev (Ber. 1911, 44, 2932; 1912, 45, 3256; Biochem. Zeitsch. 1912, 46, 483), are acted on by yeast. Glycerol, and the higher alcohols such as mannitol and dulcitol, are not fermented. In 1911, Neuberg (Biochem. Zeitsch. 1911, 31, 170) made the important discovery that yeast decomposes α-ketonic acids $R{\cdot}CO{\cdot}COOH$ quantitatively into carbon dioxide and the corresponding aldehyde (*see* p. 151). Many hydroxy-acids are also slowly attacked by yeast, among these being lactic acid (Buchner and Meisenheimer, Ber. 1904, 37, 417; 1905, 38, 620; 1906, 39, 3201; Oppenheimer, Zeitsch. physiol. Chem. 1914, 89, 45), glyceric acid (Neuberg and Tir, 1911, 32, 323; Lebedev, Ber. 1914, 47, 660), gluconic acid, and glyoxylic acid (Lebedev, Biochem. J. 1918, 12, 81).

2. *The rate of fermentation by yeast* has been investigated by many authors. It is best examined by Slator's method of adding a suspension of yeast to the solution to be fermented, and determining the initial rate of fermentation. In this way, all errors due to change in the amount and condition of the yeast and to the influence of the products of decomposition are, to a large extent, avoided (Chem. Soc. Trans. 1906, 128). By this and other methods, it has been established that (1) the rate of fermentation is directly proportional to the number of yeast cells present; (2) the rate of fermentation increases with the concentration of the sugar up to a certain limit, and then remains approximately constant, decreasing slightly as the concentration is further augmented.

Working with a suspension of 40,000,000 cells of brewery yeast per c.c. at 30°, Slator found that the rate was almost constant for glucose concentrations between 0·5 and 10 grams per 100 c.c. The mode of action of yeast is therefore identical with that typical of enzymes which has already been discussed.

The rate increases with the temperature, but the temperature coefficient diminishes as the temperature increases. The following values were obtained by Slator for glucose; they are independent of the concentration of yeast and glucose, the class of yeast and presence and absence of nutrient materials, remaining the same when inhibiting agents are present:—

Temp.	V_{t+10}/V_t
5°	5·6
10°	3·8
15°	2·8
20°	2·25
25°	1·95
30°	1·6

The temperature coefficient for an ordinary chemical reaction is of the same order as these numbers, viz. 2–3 for 10°.

Glucose and fructose are fermented at the same rate, and this is also the case when the fermenting power of the yeast is partially destroyed by heat, antiseptics, &c. On the other hand, mannose and galactose may be fermented at a different rate from glucose, and the rates are differently affected by inhibiting agents. The temperature coefficients for fructose and mannose are the same as for glucose, that for galactose is slightly less.

3. *Heat of fermentation.* During the fermentation of sugar by yeast, a considerable amount of heat is evolved, so that the temperature of the mass rises as the fermentation proceeds. The quantity of heat evolved may be calculated from the difference between the heat of combustion of glucose (675·7 Cals.) and that of the alcohol formed from it ($2 \times 325{\cdot}7 = 651{\cdot}4$ Cals.), the remaining product, the carbon dioxide, being completely oxidised. This difference amounts to 22·3 Cals., so that the fermentation of 180 grams of glucose liberates enough heat to raise the temperature of 22 litres of water 1°. This theoretical number has been confirmed by the experiments of Bouffard (Compt. rend. 1895, 121, 357), who obtained the value 23·5 Cals. In the fermentation of a disaccharide, heat is also evolved by the hydrolysis to the simple sugars;

but this is small in amount, being 4·5 Cals. for cane sugar and 3·8 Cals. for maltose (Herzog, Zeitsch. physiol. Chem. 1903, 37, 383), so that the numbers actually observed for these sugars per gram-molecule are approximately twice that for glucose (Rubner, Arch. Hygien. 1904, 48, 260; 49, 355; A. J. Brown, J. Inst. Brewing, 1901, 7, 93).

4. *Products of fermentation.* The earlier observers (Lavoisier, Gay-Lussac) considered that in the process of fermentation the sugar was completely decomposed into carbon dioxide and alcohol, according to the equation:

$$C_6H_{12}O_6 = 2CO_2 + 2C_2H_6O$$

Schmidt, in 1847, however, observed the occurrence of succinic acid in all fermented liquors, and the amount of this substance formed was carefully estimated by Pasteur (Compt. rend. 1858, 46, 857), who also made the important observation that glycerol was an invariable product of the fermentation of sugar. According to Pasteur, the products from 100 parts of cane sugar, which yield 105·36 parts of invert sugar, are:

Alcohol	51·11
Carbon dioxide . . .	49·42
Succinic acid	0·67
Glycerol	3·16
Cellulose, fat, and extractive matter	1·00
	105·36

The proportions of these products were subsequently found to be variable and to depend on the condition of the yeast, the nature of the nutrient material, &c. Many other subsidiary products have now been recognised in addition to succinic acid and glycerol. Among these may be mentioned *iso*butyleneglycol (in wine and cherry brandy), formic acid, acetic acid, propionic acid, butyric acid, and several still higher acids, which occur as esters (caproic, caprylic, pelargonic, capric, œnanthylic), and formaldehyde, acetaldehyde, and traces of higher aldehydes, propyl alcohol, *n*-butyl alcohol, *iso*butyl alcohol, *n*-amyl alcohol, *iso*-amyl alcohol, ethylmethylcarbinol, and alcohols containing 6, 7, and 9 carbon atoms.

The alcohols and aldehydes mentioned above are found in the spirit obtained by the distillation of the fermented liquids. All such spirit yields a fraction of high boiling-point, which amounts to 0·1–0·7 p.c. of the whole, and is known as fusel oil (*q.v.*). The discussion which has long raged over the origin of this fusel oil has been set at rest by the researches of Ehrlich (Zeitsch. Rüb. Zuck. Ind. 1905, 539; Biochem. Zeitsch. 1906, 2, 52; 1909, 18, 391; Ber. 1906, 39, 4072; and many other papers), who has proved in the most conclusive manner that the higher alcohols and probably the corresponding acids and aldehydes which are observed in fermented liquids are formed by the yeast, not from the sugar, but from the amino-acids produced by the hydrolysis of the proteins of the medium and of the yeast cell itself.

The reaction is a general one, and requires the presence of living yeast and sugar as well as the amino-acid. Under these circumstances, the yeast not only ferments the sugar to alcohol and carbon dioxide in the usual way, but also brings about what Ehrlich terms the alcoholic fermentation of the amino-acids, according to the equation:

$$R{\cdot}CH(NH_3){\cdot}COOH + H_2O = R{\cdot}CH_2{\cdot}OH + NH_3 + CO_2$$

The ammonia appears to be invariably assimilated by the yeast and is not found in the medium. This fact probably affords the key to the biological significance of the reaction. It is by means of this change that the yeast acquires the nitrogen necessary for its existence from the amino-acids, which are usually the chief available source of this element. The whole change is rendered possible by the utilisation of some of the energy evolved by the fermentation of sugar, which is proceeding simultaneously. Ehrlich has shown, by careful experiments, that in this way, leucine

$$(CH_3)_2{\cdot}CH{\cdot}CH_2{\cdot}CH(NH_2){\cdot}COOH$$

yields the *iso*amyl alcohol

$$(CH_3)_2{\cdot}CH{\cdot}CH_2{\cdot}CH_2(OH)$$

and *iso*leucine $C_2H_5{\cdot}CH(CH_3){\cdot}CH(NH_2){\cdot}COOH$ the *d*-amyl alcohol $C_2H_5{\cdot}CH(CH_3){\cdot}CH_2{\cdot}OH$, which are the main constituents of fusel oil.

The other amino-acids yield corresponding products, tyrosine

$$OH{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH(NH_2){\cdot}COOH$$

being converted into *p*-hydroxyphenylethyl alcohol or tyrosol $OH{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, a substance of intensely bitter taste, and phenylalanine $C_6H_5{\cdot}CH_2{\cdot}CH(NH_2){\cdot}COOH$ into phenylethyl alcohol $C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, one of the chief constituents of oil of roses. It is almost certain that many of the substances which impart flavour, bouquet, and aroma to fermented liquors have their origin in this manner, so that the subject is one of fundamental importance for the technologist.

Succinic acid is also formed by a reaction of this kind, which differs from the foregoing in so far as it involves an oxidation. The source of this substance is glutamic acid

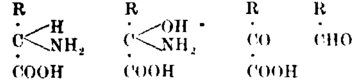
$$COOH{\cdot}CH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}COOH$$

which, instead of yielding γ-hydroxybutyric acid, as might have been expected, is converted into succinic acid

$$\begin{aligned}&COOH{\cdot}CH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}COOH + 2O\\&\quad = COOH{\cdot}CH_2{\cdot}CH_2{\cdot}COOH + CO_2 + NH_3\end{aligned}$$

Yeast is, moreover, not only capable of producing these changes in amino-acids naturally present in the medium or purposely added to it, but also decomposes in a similar manner the amino-acids formed by the hydrolysis of its own albumin. Some of the cells evidently utilise the products of the autolysis of others which have died, and hence it comes about that even when a pure sugar solution is fermented by pure washed yeast, the fermented liquid contains a certain small proportion of fusel oil, succinic acid, &c. The amounts produced in these circumstances are, however, small, as they are also when the yeast is grown in presence of ammonium salts. It also follows from this that when yeast is grown in a synthetic medium, containing ammonium salts only as the source of nitrogen, the carbon of any fusel oil or succinic acid produced is indirectly derived from the sugar.

It seems probable, from the experiments of Neubauer and Fromherz (Zeitsch. physiol. Chem. 1911, 70, 326), that the amino-acid (I.) first undergoes indirect oxidation to the corresponding ketonic acid (III.) and ammonia, and that the acid is then decomposed by the yeast, forming carbon dioxide and an aldehyde (IV.), which then either undergoes reduction to an alcohol (*e.g.* fusel oil) or oxidation to an acid (*e.g.* succinic acid).



I. II. III. IV.

It is interesting to note that the reaction proceeds asymmetrically as already described (*see Enzyme action*).

It has now been proved by Neuberg and his colleagues (*v. post*) that the glycerol, which is invariably formed during fermentation, and, unlike the substances discussed above, is equally produced by yeast juice and zymin in the absence of living yeast, is derived from the sugar.

The production of by-products is influenced not only by the nature of the available nitrogen supply, as already explained, but also by many other factors. Thus, Ashdown and Hewitt (Chem. Soc. Trans. 1910, 636) have adduced evidence to show that in the presence of formates the amount of aldehyde produced diminishes.

5. *Ratio of alcohol to carbon dioxide.* All these decompositions have an influence on the ratio of alcohol to carbon dioxide produced by alcoholic fermentation. The theoretical ratio is 46/44=1·045, and Pasteur, as quoted above, actually found 51·11 parts of alcohol to 49·42 of carbon dioxide from 100 of cane sugar. He, however, considered that succinic acid and glycerol were formed according to the equation:

$$49C_6H_{12}O_6+30H_2O = 12C_4H_6O_4+72C_3H_8O_3+30CO_2$$

and therefore ascribed 0·53 of carbon dioxide to the fermentation which had produced 0·67 of succinic acid, thus leaving 48·89 of carbon dioxide as the product of the true alcoholic fermentation, the corrected ratio being thus 51·11/48·89=1·045, exactly the theoretical. Similar results were obtained by Jodlbauer (Zeitsch. Rüb. Zuck. Ind. 1888, 308), who found that cane sugar yielded 49·04 p.c. of carbon dioxide.

Buchner and Meisenheimer (Ber. 1910, 43, 1773), working with pure yeast (Race 792 of the Berlin Collection), obtained 49·73 p.c. of the cane sugar as alcohol, and 49·12 p.c. as carbon dioxide, the ratio being 1·01. They ascribe this excess of carbon dioxide to the oxidation corresponding to the production of glycerol, the amount of which was not estimated. In spite of the fact that no nitrogenous material was added to the medium, the carbon dioxide and alcohol only represent 98·85 parts of the 105·36 of invert sugar to be accounted for, so that 6·51 parts had undergone some other change. Any carbon dioxide formed from amino-acids produced by autolysis would be included in the amount found.

6. ***Formation of glycogen: autofermentation of yeast.*** Yeast very readily converts a portion of the carbohydrate present in the medium into glycogen $C_6H_{10}O_5$, which is stored in the cell (*see* Harden and Young, Chem. Soc. Trans. 1902, 1224, where the literature is cited).

This material acts as a reserve carbohydrate, and, when the yeast is preserved in absence of sugar solution, is slowly broken down by a diastatic enzyme into sugar, and fermented into alcohol and carbon dioxide: this phenomenon is known as the autofermentation of yeast. As yeast may contain as much as 30–40 p.c. of its dry weight of glycogen, it follows that a very considerable amount of carbon dioxide and alcohol may be produced from yeast alone. The autofermentation proceeds more rapidly at high temperatures (Harden and Rowland, Chem. Soc. Trans. 1901, 1227), and is greatly accelerated by the addition of many salts (Harden and Paine, Chem. Soc. Proc. 1911, 103) and of toluene. The conditions of formation of glycogen have been investigated quantitatively by Pavy and Bywaters (J. Physiol. 1907, 36, 149), and microscopically by Wager and Peniston (Annals of Botany, 1910, 24, 45; J. Inst. Brewing, 1911–2).

The alcoholic enzyme of yeast. Attention has already been called to the fact that up to 1897 all attempts to isolate from a yeast an enzyme capable of producing alcoholic fermentation had failed. It had early been shown, at first by Mitscherlich (1841) and then by Helmholtz, that the process of fermentation in all probability took place within the cell and the efforts of later investigators had been rightly directed towards the extraction of an enzyme by some process of disintegration or treatment with solvents. All such efforts were, however, made in vain, as were also attempts to extract the enzyme by freezing or plasmolysis, the products obtained being either inactive or owing what activity they possessed to the presence of unbroken yeast cells or bacteria (Lüdersdorff, Schmidt, Pasteur, Marie von Manassëin, Adolf Mayer, Nägeli, and Loew). A slight modification of the grinding processes which had been used by several of these authors, led, however, to success. Hans and Eduard Buchner applied to yeast the process of grinding with sand which they had previously employed successfully for bacteria. By adding kieselguhr, at the suggestion of Hahn, to the pasty mass obtained, and submitting the mixture to a high pressure, they obtained a clear liquid which was capable of fermenting sugar (Buchner, Ber. 1897, 30, 117).

The nature of the active agent in yeast juice. Buchner at once established the facts that the yeast juice, prepared as just described, was capable in the absence of yeast cells of producing alcoholic fermentation, and that this power was not removed by the addition of chloroform, benzene, or sodium arsenite, by precipitation with alcohol, by evaporation to dryness at 30°–35°, or by filtration through a Berkefeld candle, whereas it was completely destroyed at 50°. He therefore concluded that the fermentative power of the juice was due to a dissolved substance of the nature of an enzyme to which he gave the name of zymase. Several of the properties of this liquid, however, suggested to various investigators that it did not contain an enzyme of the ordinary kind, but rather fragments of the living protoplasm of the yeast, which retained for some time the functions which they had possessed in the cell. This idea was in harmony with the facts that the fermenting power of the juice was rapidly lost on preservation, and that comparatively large amounts of certain antiseptics did undoubtedly greatly diminish its activity. Other objections, founded on the behaviour of the juice on dilution, &c., proved not to be well founded. Further experience of the nature of yeast juice has shown that this idea has little to recommend it. The action of antiseptics is closely analogous to their effect on other enzymes, and the loss of fermenting power has been shown to be a very complex phenomenon. No evidence of the existence in the juice of undissolved protoplasmic fragments has been put forward, and experiments on the precipitation of the juice by alcohol and ether show that if these fragments do exist they are able to withstand repeated solution in water or dilute glycerol and reprecipitation without losing their power of producing fermentation. Such properties are only consistent with the presence of an enzyme, and there seems at present no reason to doubt the existence of such an agent in yeast juice.

Preparation and properties of yeast juice. Fresh brewery yeast is washed and pressed out at about 50 kilos. per sq. cm. The resulting mass, which contains about 70 p.c. of water, is mixed with an equal weight of sand, and from 0·2–0·3 part of kieselguhr, care being taken that this is free from acid. The dry powder thus formed is then ground in small portions at a time in a large porcelain mortar by means of a heavy pestle, until the mass becomes pasty, which occurs after about 1–2 minutes' grinding. The paste is then either directly pressed out after being wrapped in a filter cloth, the pressure being gradually raised to 90 kilos per sq. cm. (Buchner), or is mixed with more kieselguhr and the dry powder pressed out between layers of chain cloth (MacFayden, Morris, and Rowland).

The yield of juice obtained from 1000 grams of bottom yeast by Buchner is about 320–460 c.c.; that obtained from English top yeasts is rather smaller, averaging 250 c.c. (Harden and Young). The product, after any suspended yeast cells have been removed by filtration or centrifugalisation, is a slightly viscid, brownish-yellow, opalescent, faintly acid liquid of sp.gr. 1·03–1·06. It contains about 8·5–14 p.c. of dissolved solids, and 0·7–1·7 p.c. of nitrogen, nearly all in the form of albumin, so that the liquid coagulates when heated. The ash amounts to 1·4–2 p.c. and, like that of yeast, contains a large proportion of phosphoric oxide.

An active extract, known as maceration juice, has been obtained by Lebedev (Compt. rend. 1911, 152, 49; Ann. Inst. Pasteur, 1912, 26, 8) by drying yeast at 25°–30°, and then macerating the dried material with 3 parts of water for 2 hours at 35°. The liquid is then filtered or centrifuged and a clear active extract is thus obtained. With some yeasts, and notably with many English top yeasts, the process fails, whereas bottom yeasts in general give good results. The extract closely resembles yeast juice obtained by grinding, but usually contains a larger amount of inorganic phosphate and a much smaller amount of glycogen.

When the juice is preserved, the protein becomes hydrolysed owing to the presence of a powerful tryptic enzyme, known as *yeast endotryptase*. At the same time, the power of producing alcoholic fermentation is lost, and it seems probable that this is due to the action of the tryptic enzyme on the alcoholic enzyme (Buchner). When excess of sugar is added and the mixture incubated at 25°, a steady fermentation ensues, carbon dioxide being evolved and alcohol produced in nearly the theoretical ratio, at a rate which gradually decreases until the process stops, after 72–96 hours, not from exhaustion of the sugar, but owing to the destruction of the active agent of fermentation. The juice from bottom yeasts appears to be more stable and to produce a somewhat greater total fermentation than that from top yeasts, 25 c.c. of juice producing on the average at 25° an evolution of about 1–1·5 grams of carbon dioxide in the case of bottom yeast, and 0·5–1 gram in the case of top yeasts.

The juice ferments those sugars which are fermentable by the yeast from which it is prepared and, in addition, dextrin, soluble starch, and glycogen, the first of which is only slowly and imperfectly fermented by yeast, and the last two not at all, as already explained. Maltose and cane sugar are hydrolysed before being fermented, and the fermentation proceeds just as with the simple sugars, glucose, fructose, and mannose. Slight differences between the rates of fermentation and the total fermentations produced with these three sugars, have been observed by Harden and Young. A yeast, which ferments galactose, yields a juice which also ferments this sugar, but the action is often much less pronounced relatively to that on glucose than is that of the living yeast (Harden and Norris).

Yeast juice, like living yeast, exhibits the phenomenon of autofermentation, which is carried out at the expense of the glycogen present in it. A diastatic enzyme, capable of hydrolysing glycogen, exists in the juice (*glycogenase*), and hence added glycogen is also fermented, but usually at a lower rate and with a smaller total yield of gas than glucose. The autofermentation of the juice from top yeast is often very considerable in amount, and may even occasionally equal that produced with glucose, whilst it is less pronounced with juice from bottom yeast. Maceration juice is almost free from autofermentation (*see* Oppenheimer, Zeitsch. physiol. Chem. 1914, 89, 63).

The rate of fermentation of sugar varies with the concentration of the sugar in the manner characteristic of enzymes, and in this respect the juice closely resembles living yeast. After a certain small limit of concentration is attained, the initial rate is practically independent of the concentration of the sugar, but decreases slightly as this increases. The gradual destruction of the enzymes produces a gradual fall in rate, which simulates the course of a monomolecular reaction, and is regarded by some investigators as evidence that the reaction is of this type (Euler, Zeitsch. physiol. Chem. 1905, 44, 53). Increased concentration of the sugar also increases both the duration of fermentation and the total fermentation, probably owing to a protective action on the fermenting mechanism.

The rate of fermentation is diminished by dilution, and, with juice of high fermenting power, is probably proportional to the concentration of the juice. The total fermentation produced is, at the same time, slightly diminished.

Accompanying the decomposition of the sugar into carbon dioxide and alcohol, a synthetic action proceeds, by which a portion of the glucose is converted into a polysaccharide, which is reconverted into glucose by hydrolysis with acid. Hence the observed loss of sugar as estimated by reducing power is usually considerably greater than the sum of the weights of alcohol and carbon dioxide produced. (This phenomenon is, however, differently interpreted by Euler; *see* Harden and Young, Biochem. J. 1913, 7, 630, where the subject is discussed.) The exact nature of this complex saccharide has not yet been determined, but observations by Cremer (Ber. 1899, 32, 2062) point to the possibility of the synthetic production of glycogen in yeast juice. As already mentioned, succinic acid and fusel oil are not formed by yeast juice, whereas glycerol is produced to the extent of about 3·8 p.c. of the sugar fermented.

The action of antiseptics on yeast juice has been investigated in some detail. Saturation with chloroform or toluene or the addition of 1 p.c. of thymol has practically no effect, whilst the inhibiting action of substances like phenol, formaldehyde, benzoic acid, and salicylic acid, is very small in 0·1 p.c. solution, more considerable in more concentrated solutions. The fermenting power is destroyed by 4 p.c. chloral, 1·2 p.c. phenol, 2 p.c. sodium fluoride, 0·55 p.c. ammonium fluoride, or 1·2 p.c. hydrocyanic acid; but in this last case it is restored when the hydrocyanic acid is removed by a current of air. The action of potassium arsenite is somewhat complex, and is treated later.

Fermentation by dry preparations of yeast and yeast juice. Yeast juice can be evaporated to dryness at 37° without loss of fermenting power as measured by the total fermentation produced. When the juice is brought into 10 volumes of acetone and rapidly drained, washed with ether, and dried, a white powder is obtained, which is almost completely soluble in dilute glycerol, and retains the fermenting power of the original juice. Dry preparations can also be obtained from yeast without any previous grinding, either by drying the yeast in air and then heating it to 100° for 6 hours (*hefanol*) or by treating it twice with a large volume of acetone (or alcohol and ether), washing with ether and drying. The material prepared in the latter way amounts to about 30 p.c. of the pressed yeast taken, and is known as acetone yeast, permanent yeast (*Dauer-hefe*) or zymin, and is almost anhydrous, sterile, and quite incapable of growth, but readily produces alcoholic fermentation when brought into sugar solution. The general phenomena of fermentation by its means are the same as are produced by yeast juice. Both the total fermentation and the rate of fermentation are 4–6 times greater than would be obtained with the yeast juice prepared from the same weight of yeast.

The conditions of action of the fermenting agent contained in yeast juice. The investigation of the mode of action of yeast juice on sugar has shown that the process is very complex. The enzyme is accompanied by another substance, termed the *coenzyme*, the presence of which is essential for the production of fermentation, and, moreover, the chemical change is not a simple decomposition of sugar, according to Gay-Lussac's equation, but a complicated reaction in which a salt of phosphoric acid takes part (Harden and Young, Proc. Roy. Soc. B. 1906, 77, 405, 78, 369; 1908, 80, 299; 1909, 81, 336; 1910, 82, 321).

The coenzyme of yeast juice. When yeast juice is passed under pressure through a Martin filter, which consists of a Chamberland filtering candle impregnated with 7–10 p.c. gelatin, all the colloidal matter of the juice is retained on the filter, whilst the dialysable substances pass through, so that the constituents of the juice are divided into two parts. When these two portions, the residue and the filtrate, are separately incubated with sugar solution, it is found that neither of them is capable of producing fermentation. When, however, the two solutions are mixed, fermentation proceeds at almost the same rate as with the original yeast juice (Harden and Young). Yeast juice, therefore, contains a dialysable substance essential for the process of fermentation, and this is provisionally termed the *coenzyme* or *coferment*. It is also present in zymin, from which it can be readily removed by simple washing with water, a perfectly inactive residue being left.

Our present information with regard to the coenzyme may be summarised as follows: (1) It is thermostable, and is not destroyed when its solution is boiled. It is therefore present in the liquids obtained by boiling yeast juice and filtering, by heating yeast at 100°, or by boiling zymin with water and filtering, and is best prepared by one of these methods. (2) It is dialysable, and can be removed from yeast juice by dialysis against water (Buchner and Antoni, Zeitsch. physiol. Chem. 1905, 46, 136) as well as by the filtration methods already described. (3) It is destroyed by hydrolysis by acids or alkalis, and even by the continued boiling of its solution. (4) It is gradually destroyed in yeast juice, less rapidly in presence of sugar, by an enzyme, which appears to belong to the group of lipases, since the destruction proceeds more rapidly in the presence of the lipase of castor-oil seeds, but is not accelerated by trypsin (Buchner and Klatte, Biochem. Zeitsch. 1908, 8, 520). (5) It is not precipitated or destroyed by lead acetate, and can therefore be, to some extent, purified by means of this reagent (Harden and Young). It is precipitated by a large volume of acetone or alcohol along with the enzyme and also by colloidal ferric hydroxide (Resenscheck, Biochem. Zeitsch. 1908, 15, 11). The coenzyme is also present in animal tissues (Meyerhof, Zeitsch. physiol. Chem. 1918, 101, 165; 102, 1).

It was found by Oppenheimer (Zeitsch. physiol. Chem. 1915, 93, 235) that pyruvic acid and its salts, and to a smaller extent acetaldehyde, exerted a stimulating action on the fermentation of glucose by maceration juice, and Neuberg (Biochem. Zeitsch. 1915, 71, 1) extended this observation to other α-ketonic acids. Moreover, by adding a mixture of a large number of α-ketonic acids (along with a phosphate) to maceration juice inactivated by dialysis, or zymin inactivated by washing, he obtained a small amount of fermentation and concluded that this mixture could partly replace the coenzyme (Neuberg and Schwenk, Biochem. Zeitsch. 1915, 71, 135). Hardon (Biochem. J. 1917, 11, 64) subsequently found that acetaldehyde was capable, in presence of potassium phosphate, of reactivating washed zymin, prepared from English top yeast. This result is, however, not accepted by Neuberg (Biochem. Zeitsch. 1918, 88, 145). He also found that the presence of K or NH_4 ions was necessary for the process, and that these could not be replaced by Na ions. Pyruvic acid, which is converted by the carboxylase of the zymin into acetaldehyde, has a similar effect. It seems possible, therefore, that the coenzyme may turn out to be acetaldehyde or some analogous substance. Neuberg and his colleagues (Biochem. Zeitsch. 1918, 88, 145; 1920, 161, 239, 276; 109, 290; 1921, 120, 215) have found that a large number of reducible substances, both inorganic and organic, act as stimulants to alcoholic fermentation by yeast preparations, and in some cases by living yeast, and consider that they act as acceptors for hydrogen, and thus increase the rate of the reaction. Harden and Henley (Biochem. J. 1920, 14, 642; 1921, 15, 175) have found that, at all events in certain cases, the stimulation is limited to the reaction in presence of phosphate (see below). Stimulation is also produced by certain substances which are not easily reducible, such as the higher polyatomic alcohols (Neuberg).

The function of phosphates in alcoholic fermentation. The addition of a soluble phosphate to a fermenting mixture of yeast juice and sugar produces a remarkable effect. The rate of fermentation is greatly increased, gradually attains a maximum, and remains at this high value for a certain time, after which it rapidly falls until it is again approximately the same as before the addition of phosphate. During this period of enhanced fermentation, the amounts of carbon dioxide and alcohol produced exceed those which would have been formed in the absence of added phosphate by an amount exactly equivalent to the phosphate added in the ratio $R_2HPO_4 : CO_2 + C_2H_6O$ (Harden and Young, Chem. Soc. Proc. 1905, 21, 189). The phosphate is, at the same time, converted into a phospho-organic compound, termed a *hexosediphosphate*, of the formula $C_6H_{10}O_4(PO_4R_2)_2$, which is not precipitated by magnesium citrate mixture or uranium salts (Harden and Young; Ivanov, Zeitsch. physiol. Chem. 1907, 50, 281). In other words, a definite chemical reaction occurs according to the following equation, which is founded on the ratio both of sugar and phosphate to carbon dioxide and alcohol, and on the composition of the hexosephosphate produced:

$$(1)\ 2C_6H_{12}O_6+2R_2HPO_4 \\ =2CO_2+2C_2H_6O+2H_2O+C_6H_{10}O_4(PO_4R_2)_2$$

In presence of excess of sugar the esterification proceeds according to a monomolecular reaction, and is most rapid in faintly alkaline reaction (Euler and Kullberg).

The existence of this reaction renders it probable that phosphates are essential for the alcoholic fermentation of the sugars by yeast juice, and that in their absence no fermentation can occur. This conclusion has been confirmed in a very striking manner by experiment. By making use of the methods described under the heading of the coenzyme, a mixture of enzyme, coenzyme, and sugar can be prepared which contains no free phosphate or hexosephosphate and very little phosphorus in any form which can yield phosphate by enzymic action. Such a mixture is almost completely devoid of fermenting power, but ferments readily when a small proportion of phosphate is added. In a particular case, the phosphate-free mixture only gave 1·5 c.c. of carbon dioxide, whereas in presence of phosphate 132 c.c. were produced (Harden and Young, Proc. Roy. Soc. B. 1911, 83, 451). As the result of the reaction expressed by equation (1), practically the whole of the free phosphate of the juice is converted into hexosephosphate, and the fermentation should therefore come to a close unless some means of regeneration of free phosphate were provided. Actually the necessary phosphate is supplied by the hydrolysis of the hexosephosphate, which is effected by an enzyme, termed on this account *hexosephosphatase*, and yields a hexose and a phosphate:

$$(2)\ C_6H_{10}O_4(PO_4R_2)_2+2H_2O \\ =C_6H_{12}O_6+2R_2HPO_4$$

Both the hexose and the phosphate thus formed enter again into reaction (1). The phosphate thus goes through a regular cycle of changes, being first converted into hexosephosphate and then liberated by hydrolysis.

It is now possible to understand the conditions which prevail in yeast juice in the presence and absence of added phosphate. When the proper or optimum amount of phosphate is added, reaction (1) proceeds at its maximum rate, and this rate affords a measure of the concentration of the fermenting complex present in the juice. When all the phosphate has been converted into hexosephosphate, the rate falls to a low level, which represents the rate at which phosphate is being supplied by the hydrolysis of the hexosephosphate. The rate of fermentation under these conditions, the so-called normal rate of fermentation, is therefore a measure of the concentration of the hexosephosphatase. If it were possible to accelerate the rate of action of this enzyme to such an extent that the supply of phosphate was maintained at the optimum amount, the rate of fermentation would be permanently maintained at the high level observed in presence of added phosphate. Precisely this result is attained by the addition of a small amount of sodium arsenate to the juice. A large and permanent rise of rate occurs, and direct experiment shows that this is due to acceleration of the rate of action of the hexosephosphatase (*see also* Meyerhof, Zeitsch. physiol. Chem. 1918, 102, 185). Arsenites produce a somewhat similar but much less marked effect (Harden and Young, *l.c.*).

Hexosediphosphoric acid. The phospho-organic compound produced during fermentation, which was first observed by Harden and Young, has since been studied by Ivanov (*l.c.* and Cent. Bakt. Par. ii. 1909, 24, 1); Lebedev (Biochem. Zeitsch. 1909, 20, 114; 1910, 28, 213; 1911, 36, 248; 1912, 39, 155; Zeitsch. physiol. Chem. 1911, 75, 499; 1913, 84, 305); Young (Proc.

dilution, and, with juice of high fermenting power, is probably proportional to the concentration of the juice. The total fermentation produced is, at the same time, slightly diminished.

Accompanying the decomposition of the sugar into carbon dioxide and alcohol, a synthetic action proceeds, by which a portion of the glucose is converted into a polysaccharide, which is reconverted into glucose by hydrolysis with acid. Hence the observed loss of sugar as estimated by reducing power is usually considerably greater than the sum of the weights of alcohol and carbon dioxide produced. (This phenomenon is, however, differently interpreted by Euler; *see* Harden and Young, Biochem. J. 1913, 7, 630, where the subject is discussed.) The exact nature of this complex saccharide has not yet been determined, but observations by Cremer (Ber. 1899, 32, 2062) point to the possibility of the synthetic production of glycogen in yeast juice. As already mentioned, succinic acid and fusel oil are not formed by yeast juice, whereas glycerol is produced to the extent of about 3·8 p.c. of the sugar fermented.

The action of antiseptics on yeast juice has been investigated in some detail. Saturation with chloroform or toluene or the addition of 1 p.c. of thymol has practically no effect, whilst the inhibiting action of substances like phenol, formaldehyde, benzoic acid, and salicylic acid, is very small in 0·1 p.c. solution, more considerable in more concentrated solutions. The fermenting power is destroyed by 4 p.c. chloral, 1·2 p.c. phenol, 2 p.c. sodium fluoride, 0·55 p.c. ammonium fluoride, or 1·2 p.c. hydrocyanic acid; but in this last case it is restored when the hydrocyanic acid is removed by a current of air. The action of potassium arsenite is somewhat complex, and is treated later.

Fermentation by dry preparations of yeast and yeast juice. Yeast juice can be evaporated to dryness at 37° without loss of fermenting power as measured by the total fermentation produced. When the juice is brought into 10 volumes of acetone and rapidly drained, washed with ether, and dried, a white powder is obtained, which is almost completely soluble in dilute glycerol, and retains the fermenting power of the original juice. Dry preparations can also be obtained from yeast without any previous grinding, either by drying the yeast in air and then heating it to 100° for 6 hours (*hefanol*) or by treating it twice with a large volume of acetone (or alcohol and ether), washing with ether and drying. The material prepared in the latter way amounts to about 30 p.c. of the pressed yeast taken, and is known as acetone yeast, permanent yeast (*Dauer-hefe*) or zymin, and is almost anhydrous, sterile, and quite incapable of growth, but readily produces alcoholic fermentation when brought into sugar solution. The general phenomena of fermentation by its means are the same as are produced by yeast juice. Both the total fermentation and the rate of fermentation are 4–6 times greater than would be obtained with the yeast juice prepared from the same weight of yeast.

The conditions of action of the fermenting agent contained in yeast juice. The investigation of the mode of action of yeast juice on sugar has shown that the process is very complex. The enzyme is accompanied by another substance, termed the *coenzyme*, the presence of which is essential for the production of fermentation, and, moreover, the chemical change is not a simple decomposition of sugar, according to Gay-Lussac's equation, but a complicated reaction in which a salt of phosphoric acid takes part (Harden and Young, Proc. Roy. Soc. B. 1906, 77, 405, 78, 369; 1908, 80, 299; 1909, 81, 336; 1910, 82, 321).

The coenzyme of yeast juice. When yeast juice is passed under pressure through a Martin filter, which consists of a Chamberland filtering candle impregnated with 7–10 p.c. gelatin, all the colloidal matter of the juice is retained on the filter, whilst the dialysable substances pass through, so that the constituents of the juice are divided into two parts. When these two portions, the residue and the filtrate, are separately incubated with sugar solution, it is found that neither of them is capable of producing fermentation. When, however, the two solutions are mixed, fermentation proceeds at almost the same rate as with the original yeast juice (Harden and Young). Yeast juice, therefore, contains a dialysable substance essential for the process of fermentation, and this is provisionally termed the *coenzyme* or *co-ferment.* It is also present in zymin, from which it can be readily removed by simple washing with water, a perfectly inactive residue being left.

Our present information with regard to the coenzyme may be summarised as follows: (1) It is thermostable, and is not destroyed when its solution is boiled. It is therefore present in the liquids obtained by boiling yeast juice and filtering, by heating yeast at 100°, or by boiling zymin with water and filtering, and is best prepared by one of these methods. (2) It is dialysable, and can be removed from yeast juice by dialysis against water (Buchner and Antoni, Zeitsch. physiol. Chem. 1905, 46, 136) as well as by the filtration methods already described. (3) It is destroyed by hydrolysis by acids or alkalis, and even by the continued boiling of its solution. (4) It is gradually destroyed in yeast juice, less rapidly in presence of sugar, by an enzyme, which appears to belong to the group of lipases, since the destruction proceeds more rapidly in the presence of the lipase of castor-oil seeds, but is not accelerated by trypsin (Buchner and Klatte, Biochem. Zeitsch. 1908, 8, 520). (5) It is not precipitated or destroyed by lead acetate, and can therefore be, to some extent, purified by means of this reagent (Harden and Young). It is precipitated by a large volume of acetone or alcohol along with the enzyme and also by colloidal ferric hydroxide (Resenscheck, Biochem. Zeitsch. 1908, 15, 11). The coenzyme is also present in animal tissues (Meyerhof, Zeitsch. physiol. Chem. 1918, 101, 165; 102, 1).

It was found by Oppenheimer (Zeitsch. physiol. Chem. 1915, 93, 235) that pyruvic acid and its salts, and to a smaller extent acetaldehyde, exerted a stimulating action on the fermentation of glucose by maceration juice, and Neuberg (Biochem. Zeitsch. 1915, 71, 1), extended this observation to other α-ketonic acids. Moreover, by adding a mixture of a large number of α-ketonic acids (along with a phosphate) to maceration juice inactivated by to the effect that a preliminary partial fermentation of glucose (but not of fructose) by living yeast renders it more readily susceptible of enzymic esterification with phosphates.

Carboxylase. As mentioned above, yeast decomposes α-ketonic acids into carbon dioxide and the corresponding aldehyde

$$R{\cdot}CO{\cdot}COOH = R{\cdot}CHO + CO_2$$

This reaction is brought about by all races of brewer's yeast, and by wine yeasts, and has been traced to the presence in these of an enzyme termed by Neuberg carboxylase. From the cell this enzyme passes into yeast juice, so that this also possesses the property of decomposing α-ketonic acids. The salts are also attacked, the carbonate or bicarbonate of the metal being formed, and a certain amount of the aldehyde undergoing condensation to inactive aldol under the influence of the alkaline carbonate. The enzyme is undoubtedly distinct from zymase, and is differently affected by agents such as heat and antiseptics. Its action is, moreover, independent of the presence of the coenzyme of yeast juice (Harden, Biochem. J. 1913, 7, 214; Neuberg and Rosenthal, Biochem. Zeitsch. 1913, 51, 125).

The play of enzymes in yeast juice. It will be seen from the foregoing that the number of factors concerned in fermentation by yeast juice is very large, and that the conditions are correspondingly complex. In addition to the enzyme and coenzyme, together forming the fermenting complex, the hydrolytic enzyme hexosephosphatase, the free phosphate and the sugar, and probably the carboxylase, which are all directly involved in fermentation, a number of other agencies are at work which influence the course of the reaction. Chief among these are the hydrolytic enzymes which cause the destruction of the enzyme and coenzyme respectively. The former of these is probably proteoclastic and the latter lipoclastic, and on the relative concentration of these and of the enzyme and coenzyme themselves depends the exact course of events. During the normal fermentation in presence of excess of sugar, both the enzyme and coenzyme are gradually being destroyed, and fermentation ceases as soon as either of these has completely disappeared. In juice from top yeast, it is found that the cessation of fermentation is due to the disappearance of the enzyme. Buchner and Klatte (Biochem. Zeitsch. 1908, 8, 520) have, however, found that in juice from bottom yeast the coenzyme disappears first, and that the fermentation can be restarted by the addition of boiled yeast juice containing a fresh supply of coenzyme. The matter is even more complex than this, for boiled yeast juice has been found to contain an antiprotease (analogous to the antitrypsin of blood serum) which inhibits the action of the tryptase of the yeast, and thus preserves the enzyme from destruction. The presence of this agent is partly responsible for the considerable increase in total fermentation produced by the addition of boiled yeast juice to fresh yeast juice, the coenzyme and the phosphate added at the same time having also a share in the phenomenon. The hexosephosphatase appears always to outlast both the enzyme and coenzyme. The addition of sugar alone also exerts a protective action upon the enzymes of the juice, the power of producing fermentation being retained for a much longer time in presence than in absence of the sugar. All these phenomena of protection are probably to be referred to the formation of some sort of compound or association between the substances concerned in fermentation, which renders them less capable of reaction with other substances.

The nature of the process of fermentation in the living yeast cell. When the effects produced by yeast juice and zymin are compared with those due to living yeast, it is found that yeast juice ferments glucose at a rate which is only about $\frac{1}{40}$ of that given by the yeast from which it was prepared, whilst zymin yields a rate which is $\frac{1}{7}$–$\frac{1}{10}$ of that of yeast. In the presence of fructose and phosphate, the rate of fermentation of yeast juice may be increased as much as 20-fold, then amounting to about one-half the rate of that of living yeast, whilst that of zymin may be increased to approximately the same relative value. Assuming, as appears justified, that the process of fermentation is of the same general character in yeast as in yeast juice, it follows that yeast juice contains a large fraction of the fermenting complex present in yeast, but differs from this mainly in the power of regenerating phosphate. Zymin appears to contain a somewhat smaller proportion of the fermenting complex, but has a much greater power of regenerating phosphate than yeast juice, although still considerably less than living yeast. A similar effect to that which is produced by grinding yeast, treating it with acetone or drying and heating it, is also produced, but to a smaller degree, by treating it with toluene (Harden), so that all these processes must result in some similar change which is rendered evident by the loss of the power of regenerating phosphate from hexosephosphate. Of the nature of this change we are, at present, ignorant, but the facts strongly suggest that it is in some way due to the disorganisation of the cell. Another difference between yeast juice and yeast is that the latter does not respond, like yeast juice, to the addition of phosphate or of arsenate. This is in reality another consequence of the superior phosphate-producing power of the yeast cell, whereby the optimum amount of phosphate is constantly supplied. In presence of a constant concentration of sugar, coenzyme and phosphate, the rate of fermentation is approximately proportional to the concentration of the enzyme (Meyerhof).

In the light of what has been said, the following scheme of fermentation in the yeast cell may be imagined. The sugar first diffuses into the cell, and it has been shown by Slator and Sands that the rate of diffusion is much more than sufficient to supply the sugar necessary for fermentation, and is therefore not the controlling factor in the observed rate of fermentation (Chem. Soc. Trans. 1910, 922). Inside the cell, the sugar, either as such or having undergone some change such as conversion into the enolic form (E. F. Armstrong), combines with the fermenting complex, and is thereby brought into relation with phosphate, probably also combined with the fermenting complex. This association of fermenting complex, sugar, and phosphate then breaks down with liberation of the fermenting complex, accompanied either by the formation of carbon dioxide, alcohol, and hexosephosphate, according to equation (1) previously given, or of the products of some intermediate stage of this reaction. It is probably the rate of this decomposition which is measured as the rate of fermentation. The hexosephosphate is rapidly hydrolysed and a supply of fresh phosphate thus provided, which, along with the hexose formed at the same time, and a new quantity of sugar supplied by diffusion, again enters into association with the fermenting complex, and thus continues the fermentation.

The results obtained by Slator with mannose and the facts already related with regard to galactose, suggest the possibility that the whole mechanism, or at least some portion of it, may be specific for each sugar, but definite evidence of this has not yet been obtained.

On the other hand, the facts that hexosephosphates are not decomposed or fermented, and that phosphates are only very imperfectly esterified by living yeast, have led Neuberg (Biochem. Zeitsch. 1917, 83, 244) to the conclusion that the processes which occur in yeast juice do not represent the normal course of events in the uninjured yeast cell.

The chemical changes involved in alcoholic fermentation. Many theories have been advanced as to the stages which may be supposed to intervene between glucose and the final products of its decomposition—alcohol and carbon dioxide. Baeyer, in 1870, pointed out that the alternate removal and readdition of the elements of water might lead to an accumulation of oxygen on certain of the carbon atoms, and thus render the rupture of the carbon chain possible. Wohl has proposed a modification of this idea, which leads to the supposition that loss of water and intramolecular change result in the formation of a ketoaldehyde which undergoes hydrolysis to methylglyoxal and glyceraldehyde; the latter of which, by a similar series of changes, also forms methylglyoxal $CH_3{\cdot}CO{\cdot}CHO$. This then passes into lactic acid, and this into carbon dioxide and alcohol. This theory received a certain amount of experimental support from the fact that small quantities of lactic acid appear to be fermented by yeast juice (Buchner and Meisenheimer). The idea of the occurrence of lactic acid as a true intermediate product of alcoholic fermentation has, however, now been abandoned, largely owing to the criticisms of Slator, who pointed out that this substance should be fermented at least as quickly as glucose, and that this is not the case. The same criticism is valid against many of the 3-carbon compounds which have been proposed as intermediate products, including glyceraldehyde and dihydroxyacetone, both of which are slowly attacked by yeast, whilst dihydroxyacetone is also readily fermented by yeast juice prepared by maceration (Lebedew).

The pyruvic acid theory of fermentation. The universal presence of carboxylase in yeasts capable of producing alcoholic fermentation creates a strong presumption that the decomposition of pyruvic acid actually forms a stage in the alcoholic fermentation of sugars. The fact that the evolution of carbon dioxide from pyruvic acid commences instantly, whereas there is a considerable delay in the case of glucose (Neuberg and Rosenthal, Biochem. Zeitsch. 1913, 51, 128) is interpreted to mean that the glucose undergoes a preliminary change which requires some time and results in the formation of pyruvic acid capable of immediate decomposition. Other explanations of this delay, which is by no means invariable, can, however, be given. A number of observations have also been made by Euler and his school which have led him to the same conclusion, that some intermediate product is formed before the production of alcohol and carbon dioxide.

Pyruvic acid has actually been isolated by Fernbach and Schoen (Compt. rend. 1913, 157, 1478) from the products formed by the alcoholic fermentation of sugar in the presence of chalk; but Kerb (Ber. 1919, 52, *B*, 1795), using pure cultures of yeast, was unable to confirm this observation.

The pyruvic acid theory of alcoholic fermentation (Neubauer and Fromherz, Zeitsch. physiol. Chem. 1911, 70, 326; Neuberg and Kerb, Zeitsch. Gärungsphysiol. 1912, 1, 114; Kostytshev, Zeitsch. physiol. Chem. 1912, 79, 130) involves three stages, exemplified by the following equations:—

$$\text{(i)}\ C_6H_{12}O_6=2CH_3{\cdot}CO{\cdot}COOH+4[H];$$
$$\text{(ii)}\ 2CH_3{\cdot}CO{\cdot}COOH=2CH_3{\cdot}CHO+2CO_2;$$
$$\text{(iii)}\ 2CH_3{\cdot}CHO+4H=2CH_3{\cdot}CH_2{\cdot}OH$$

The products of decomposition of pyruvic acid by yeast being carbon dioxide and acetaldehyde, the production of alcohol from glucose by way of pyruvic acid must involve a process of reduction. That yeast possesses powerful reducing properties has long been known (philothion of Rey-Pailhade). These are shared by yeast juice and the other active preparations obtained from yeast, all of which are capable of reducing many aldehydes to alcohols and various colouring matters to their leuco-compounds, and are therefore supposed to contain a reducing enzyme or *reducase*. The intervention of this reducing enzyme of yeast in alcoholic fermentation was suggested in 1904 by Grüss (Zeitsch. ges. Brauwesen, 1904, 27, 689), and has since been supported by many workers, notably Palladin (Zeitsch. physiol. Chem. 1908, 56, 81), Kostytshev (numerous papers in Zeitsch. physiol. Chem. from 1912), and Lvov (1913). The attempts made by these investigators to show that in presence of reducible substances the fermentation of glucose was modified (Lvov; Kostytshev), or that the presence of glucose interfered with the reduction of other substances, were not conclusive. Neuberg, however (in a series of papers summarized in Ber. 1919, 52 *B*, 1677), has shown that in the presence of substances capable of combining with acetaldehyde the course of the fermentation is profoundly modified. For this purpose he employed normal sodium sulphite, which reacts with acetaldehyde according to the equation

$$C_2H_4O+Na_2SO_3+H_2O=C_2H_4O.NaHSO_3+NaOH$$

In the presence of this salt, under the most favourable conditions, only about 30 per cent. of the sugar undergoes the normal fermentation, whilst the remaining 70 per cent. yields acetaldehyde, glycerol and carbon dioxide according to the equation $C_6H_{12}O_6=C_2H_4O+C_3H_8O_3+CO_2$, or, including the sulphite,

$$C_6H_{12}O_6+Na_2SO_3+H_2O$$
$$=C_3H_8O_3+C_2H_4O.NaHSO_3+NaHCO_3$$

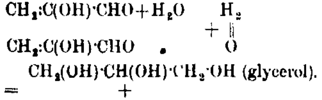
The sulphite is best added after the fermentation has commenced, from 33–150 grams being used for 100 grams cane-sugar dissolved in 1–2·5 litres of water, and about 10–20 grams of yeast. Molecular proportions of acetaldehyde and glycerol are produced throughout the whole course of the fermentation, and the yield, referred to sugar, increases with the concentration of sulphite. Insoluble sulphites (Ca, Zn, Mg) can be used if the mixture is well agitated, and the process can also be carried out in faintly acid solution in the presence of acid potassium phosphate.

An enhanced production of acetaldehyde and glycerol had previously been observed by Neuberg and Farber (Biochem. Zeitsch. 1917, 78, 238), both with living yeast and maceration juice in presence of a number of alkaline salts, but the acetaldehyde found was not chemically equivalent to the glycerol. Under these circumstances, however, it has now been found that the acetaldehyde undergoes a Cannizzaro reaction, yielding alcohol and acetic acid, so that the fermentation in presence of alkalis proceeds as follows:—

$$2C_6H_{12}O_6\rightarrow 2C_3H_8O_3+2CO_2+2C_2H_4O\xrightarrow[+H_2O]{}$$
$$2C_3H_8O_3+2CO_2+C_2H_6O+C_2H_4O_2$$

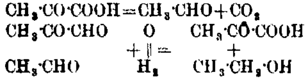
One molecule of acetic acid is thus produced for every two molecules of glycerol. The yield of glycerol obtained in this way is not so high as in the presence of sulphite, amounting in the presence of sodium bicarbonate to about 35 per cent. of the theoretical (Neuberg and Hirsch, Biochem. Zeitsch. 1919, 100, 304). Neuberg explains the results obtained, on the general lines of the pyruvic acid theory, by supposing that the sulphite combines with the acetaldehyde and thus prevents its reduction to alcohol, the glycerol being formed by the action of the hydrogen thus rendered available on the precursor of pyruvic acid, which he assumes to be methylglyoxal. According to Neuberg and Kerb (Biochem. Zeitsch. 1913, 58, 158), the normal course of fermentation takes place according to the following equations:—

(1) $C_6H_{12}O_6-2H_2O=C_6H_8O_4$ (methylglyoxal-aldol)
$=2CH_2{:}C(OH){\cdot}CHO$ or $2CH_3{\cdot}CO{\cdot}COOH$ (methylgloxal).

(2)


$$\begin{array}{ll}\mathrm{CH_2{:}C(OH){\cdot}CHO+H_2O} & \mathrm{H_2}\\ & +\ \Vert\\ \mathrm{CH_2{:}C(OH){\cdot}CHO} & \mathrm{O}\end{array} = \begin{array}{l}\mathrm{CH_2(OH){\cdot}CH(OH){\cdot}CH_2{\cdot}OH\ (glycerol).}\\ +\\ \mathrm{CH_3{\cdot}CO{\cdot}COOH\ (pyruvic\ acid).}\end{array}$$

(3) $CH_3{\cdot}CO{\cdot}COOH=CH_3{\cdot}CHO+CO_2$

(4)


$$\begin{array}{lcl}\mathrm{CH_3{\cdot}CO{\cdot}CHO} & \mathrm{O} & \mathrm{CH_3{\cdot}CO{\cdot}COOH}\\ & +\ \Vert\ = & +\\ \mathrm{CH_3{\cdot}CHO} & \mathrm{H_2} & \mathrm{CH_3{\cdot}CH_2{\cdot}OH}\end{array}$$

In the presence of sulphite or of alkalis a certain proportion of the aldehyde produced in (3) is withdrawn from the system so that reaction (4) is greatly diminished in rate and the end-products contain a large proportion of acetaldehyde and glycerol, the latter formed according to equation (2). Wo. Ostwald (Biochem. Zeitsch. 1919, 100, 279; *see also* Neuberg, *ibid.* 289) has pointed out that the enhanced production of acetaldehyde would naturally follow on the removal of this substance from the sphere of action, the equilibrium being in this way constantly disturbed, so that this fact cannot in itself be regarded as a strict proof of the theory that pyruvic acid is an intermediate product in the normal course of fermentation. In view of the fact that in the modified fermentation, the acetaldehyde is produced at approximately the same rate as alcohol in the normal fermentation there can be little doubt that Neuberg's explanation is in this particular correct.

No definite experimental evidence of the participation of methylglyoxal in the process of fermentation has yet been obtained, and it is still doubtful whether Neuberg's equations represent the actual mechanism of the fermentation. It is possible that in the decomposition of glucose by way of pyruvic acid into alcohol and carbon dioxide, either the reducase combines with hydrogen and passes it on to the aldehyde or, alternatively, and more probably, that in presence of the reducing enzyme water is decomposed, the oxygen converting glucose, or some intermediate product obtained from it, into pyruvic acid, whilst the hydrogen reduces the aldehyde to alcohol as in Neuberg's equation (4). This reaction would be continuous as soon as a supply of aldehyde had been accumulated, but would not commence except in the presence of some acceptor for the hydrogen.

Much further evidence is required before any satisfactory conclusion can be arrived at with regard to this subject, and the facts must certainly be taken into account that two molecules of sugar are involved in the reaction, and that the products include hexosephosphate as well as alcohol and carbon dioxide.

Practically the possibility of producing a large proportion of glycerol from sugar by fermentation in presence of sulphite has been made the basis of a process of manufacture of this substance (the Protol process), which has been worked on such a scale as to produce a million kilos. of glycerol per month in a yield of 20–25 per cent. of the sugar employed (Connstein and Lüdecke, Ber. 1919, 52, *B*, 1385).

FERMENTATIONS PRODUCED BY BACTERIA.

Bacteria are capable of bringing about many fermentations which are strictly analogous to the fermentation of the sugars by yeast. Many species of bacteria are, however, much less restricted in their power of action, and decompose not only the simple hexoses and complex saccharides, but also the glucosides, the lower sugars, especially the pentoses and the corresponding alcohols including glycerol, as well as many organic acids. In addition to this, they also act upon nitrogenous compounds, and effect many oxidations and reductions. The chemical changes involved are of the most varied kind, and although they are in all probability brought about by enzymes, it is only in comparatively simple cases that the enzyme has been separated from the cell. In some cases, however, the enzymes pass into the surrounding medium, this being frequently the case with the various digestive enzymes, and possibly with the urease which brings about the hydrolysis of urea into ammonium carbonate and water.

Interesting and important attempts have been made by Buchner to prepare extracts containing active enzymes from the bacteria of the lactic acid and acetic acid fermentations, by a process similar to that employed for yeast, but in both cases without success. He was able, however, to demonstrate the existence of such an enzyme in the cell by treating the organism with acetone, and showing that the dead and sterile material was still capable of converting sugar into lactic acid in the one case, and of oxidising alcohol to acetic acid in the other. Similar results have been obtained with a number of other bacteria.

Although the qualitative characteristics of the action of bacteria on many substances are well known and are largely used for purposes of identification and differentiation, comparatively little strictly quantitative work on the subject has been done, in which all the products derived from a known weight of a material have been estimated, and hence our knowledge of the chemistry of bacterial action remains very imperfect. Among the pioneers in this branch of the subject must be reckoned Fitz (who, however, often employed mixed cultures) and P. F. Frankland. The employment of mixed cultures is not entirely without justification, since many of the changes produced in nature by bacteria, such as putrefaction, are brought about by the combined or successive action of different organisms, some of which make use of the products of decomposition formed by others.

The chief types of fermentation produced by bacteria may be classified in much the same manner as those due to enzyme action, under the heads of (1) hydrolysis; (2) decomposition involving the rupture of a carbon chain; (3) oxidation; (4) reduction and deoxidation.

1. Fermentations by Hydrolysis.

A large number of bacteria contain enzymes, which enable them to bring about processes of hydrolysis, whether of proteins or carbohydrates, and in some cases these are soluble and pass into the medium.

(a) Liquefaction of gelatin. Protooclastic enzymes capable of liquefying gelatin are almost certainly present in all bacteria, but they are only excreted by certain organisms, and therefore afford a differential test often employed as an aid in identification. For this purpose, the organism is grown on nutrient gelatin, and note is taken as to whether the gelatin becomes liquefied. Prominent among the organisms which liquefy gelatin in this way are *B. fluorescens liquefaciens* (Flügge), *B. vulgaris* (Lehm. and Neum.), &c., whilst the intestinal organisms of the *B. coli* group are non-liquefiers. The liquefaction of gelatin is the first step in the hydrolysis of this substance, and is often followed by a more deep-seated decomposition of the resulting simpler compounds, which is discussed later on under the heading of *Putrefaction*. Some organisms only bring about the liquefaction of gelatin when grown in air, but do not liquefy in it an atmosphere of hydrogen or nitrogen, although growth takes place.

(b) Hydrolysis of polysaccharides and glucosides. It seems probable that most bacteria resemble yeasts in the fact that, when brought into contact with polysaccharides, they do not ferment them directly, but first hydrolyse them and then ferment the resulting simple sugars; and the same thing is true of the glucosides. In most cases no strict proof of this has been brought, but in some the hydrolysis has been actually demonstrated. Thus Bertrand and Weisweiller (Ann. Inst. Pasteur, 1906, 20, 977) found that the *B. bulgaricus* (Grig.) hydrolysed milk sugar before producing lactic acid from it, and were able to prove the existence of glucose and galactose in the partially fermented solution. The determination of the fermentability or non-fermentability of the di- and tri-saccharides, starch, dextrin, inulin, and many glucosides, is now largely employed for the identification of bacteria, especially those of the *B. coli* group and the *Streptococci*. It follows from the foregoing that what is being tested for in such cases is most probably the presence or absence of the ferment requisite for the hydrolysis in question, *e.g.* invertase by cane sugar, maltase by maltose, lactase by lactose, β-glucosidase by many glucosides, such as saligenin, amygdalin, &c.

The presence of the hydrolytic ferment is rendered evident by the subsequent fermentation of the resulting simple sugars, &c., with production of acid or evolution of gas or both. The efficacy of the test, therefore, depends on the ability of the organism to ferment at least one of the products of the hydrolysis.

(c) The ammoniacal fermentation of urea. The waste nitrogen of the animal body is excreted in the urine, chiefly in the form of urea $CO(NH_2)_2$, uric acid $C_5H_4O_3N_4$, allantoin $C_4H_6O_3N_4$, and hippuric acid

$$C_6H_5{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}COOH$$

In the urine of man, about 30 grams of urea are passed per diem, along with 0·7 gram of uric acid, and very small amounts of hippuric acid; whilst the urine of graminivorous animals contains comparatively large amounts of urea and hippuric acid (Liebig, 1829), the urine of a cow containing 18 grams of urea and 16 of hippuric acid per litre. On the other hand, the nitrogenous waste of birds and snakes is excreted almost entirely in the form of uric acid. The conversion of the nitrogen of these substances in the soil back into ammonia, which is then rendered available for plants by nitrifying organisms, is of vast importance, as it is in this way that the nitrogen balance of the soil is maintained, practically the whole nitrogen of natural manures being present in these forms.

When urine, which is normally sterile and acid in reaction, is exposed to air, it becomes alkaline, the urea being converted into ammonium carbonate:

$$CO(NH_2)_2+2H_2O=(NH_4)_2CO_3$$

This change was observed at a very early date, and was ascribed by Liebig, in accordance with his theory of fermentation, to the presence of decomposing mucus from the bladder. About 1860, however, it was established by Pasteur (Compt. rend. 1860, 50, 849), his pupil, van Tieghem (*ibid.* 1861, 52, 210; 1864, 58, 210), and Müller (J. pr. Chem. 1860, 81, 452), that the decomposition was produced by a micrococcus which was termed *Torule ammoniacale* by

Pasteur, and later *Micrococcus ureæ* by Cohn. It has since been found, as the result of numerous researches by Flügge, Heræus, Warington, Leube, Beyerinck, and especially Miquel (literature quoted in article by Miquel in Lafar, Technische Mykologie, iii. 71), that a large number of organisms have the power of producing this change. More than thirty varieties have been described by Miquel alone, who has also found that these organisms occur freely in water, air, and soil, the cocci being about twice as frequent as the bacilli, whilst 1–2 p.c. of the organisms of the Paris water, air, and cultivated soil belong to this class. The most characteristic and commonly occurring coccus is that originally discovered by Pasteur, now known as *Urococcus van Tieghemi* (Miquel), which is a small diplococcus, and grows well on ordinary media, not liquefying gelatin. In presence of urea, the growth on solid media becomes surrounded by dumb-bell-shaped crystals, which are insoluble in water, and consist of the phosphates and carbonates of calcium, precipitated from the medium by the ammonia produced. This is a very characteristic phenomenon, and renders it easy to detect not only this organism but any urea ferment among a number of organisms which do not attack urea. The organism readily decomposes as much as 4–4·5 p.c. of urea in the medium, but is very susceptible to antiseptics.

The most energetic decomposition of urea is brought about by the *Urobacillus Pasteurii* (Miquel) isolated from sewage. This is a motile, sporing bacillus, which grows well in alkaline broth, which it renders viscid and ropy. It ferments completely as much as 13 p.c. of urea in the medium, and has been observed to decompose 3·3 grams of urea per hour per litre of culture.

As early as 1876, Musculus (Compt. rend. 1874, 78, 132; 1876, 83, 333) found that the slimy urine of patients suffering from cystitis, and probably infected by the foregoing urobacillus, contained a soluble ferment which could be precipitated by alcohol and was capable of converting urea into ammonium carbonate in the absence of bacteria. Pasteur and Joubert, on the other hand, maintained that this action was due to the presence of an organism (Compt. rend. 1876, 83, 1).

The question of the existence and properties of this enzyme has been studied by many investigators (Leube, Lea, Beyerinck, Miquel, Moll) with somewhat discrepant results, ascribed by some to the unstable character of the enzyme. It can hardly, however, be considered as definitely proved that the enzyme has been obtained free from bacteria. According to Miquel, it can readily be obtained in solution by inoculating alkaline beef broth containing urea with one of the urea-fermenting organisms, and, after some time, filtering through a biscuit porcelain candle. The liquid is then sterile and capable of decomposing as much as 100–120 grams of urea per litre per hour at 48°. Its activity is greatly increased by cane sugar and glycerol, and is very readily inhibited by antiseptics. It may be precipitated by the addition of 2 volumes of alcohol. Musculus employed a turmeric paper moistened with a solution of the enzyme as a test for urea, the liberated ammonia producing a brown colour, and Miquel has proposed the use of solutions of the enzyme for the quantitative estimation of urea as ammonia. On the other hand, bacteria isolated from the root tubercles of the soya bean, which have a well-marked power of hydrolysing urea, do not yield an active filtrate (Jacoby, Biochem. Zeitsch. 1916, 74, 109). A very powerful urease exists in the soya bean and many other seeds (p. 140).

(*d*) **The fermentation of uric acid.** Uric acid readily undergoes a combined bacterial oxidation and hydrolysis, but little is known as to the nature of the bacteria which produce the change (Sestini, Gazz. chim. ital. 1889; Gérard, Compt. rend. 1896, 122, 1019; 123, 185; Ulpiani, Atti Lincei, 1903, 12, 236). It seems probable that urea is first produced and then further hydrolysed:

$$C_5H_4O_3N_4+2H_2O+3O=2CO(NH_2)_2+3CO_2$$

(*e*) **The fermentation of hippuric acid.** Van Tieghem (Compt. rend. 1864, 58, 210) showed that the same micrococcus which fermented urea also effected the hydrolysis of hippuric acid into benzoic acid and aminoacetic acid, into which it is also converted by acids:

$$C_6H_5CO{\cdot}NH{\cdot}CH_2{\cdot}COOH+H_2O$$
$$=C_6H_5{\cdot}COOH+NH_2{\cdot}CH_2{\cdot}COOH$$

It has since been found that more than one of the urea-fermenting organisms produce this change (Rattone and Valenta, Arch. Scienz. mediche, 1886, 10, 311). In the soil, the aminoacetic acid then probably undergoes one of the characteristic changes described under *Putrefaction*, its nitrogen being liberated as ammonia.

2. FERMENTATIONS BY DECOMPOSITION ACCOMPANIED BY THE RUPTURE OF A CARBON CHAIN.

The chief chemical characteristic of this form of fermentation is that it involves the rupture of the carbon chain of the fermentable substance, the products being, as a rule, substances containing a smaller number of carbon atoms than the original compound. In many cases, however, a secondary synthesis occurs, and compounds are then found among the products containing more carbon atoms in the molecule than the original substance, the best known example of this being the production of butyric acid from glycerol.

As regards the nature of the changes produced, the same intramolecular oxidation and reduction is observed as characterises the alcoholic fermentation of sugar. Carbon dioxide is very frequently evolved, and this is often accompanied by free hydrogen, less frequently by marsh gas. The hydrogen thus formed is capable of bringing about the reduction of many substances such as nitrates, amino-acids, &c., which may be present in the medium, and thus modifying the result. In many cases in which no gas is evolved, formic acid is produced in considerable quantity, and this substance is sometimes found in comparatively small amount, even when carbon dioxide and free hydrogen have been evolved. The production of ethyl alcohol is also a feature of common occurrence, and methyl, propyl, isopropyl and *n*-butyl alcohols have all been observed as well as acetone, acetylmethylcarbinol, and butyleneglycol. Among the other products, lactic acid, which has the same empirical formula as glucose, is one of the most frequent. In some cases, the conversion of a sugar into lactic acid is almost quantitative, whilst in others this acid forms only a small proportion of the whole product. Acetic acid, which also has the same empirical formula as glucose, is also a common product, and is sometimes accompanied by propionic and other of the fatty acids. Characteristic of one type of fermentation is the production of butyric acid, accompanied by more or less butyl alcohol. An almost invariable product of the bacterial fermentation of sugars and alcohols is succinic acid, probably in part derived, as in alcoholic fermentation, from the decomposition of amino-acids.

Although bacteria are much less specific in their power of fermentation than the yeasts, they nevertheless display great sensitiveness to small changes in chemical composition and configuration. Thus many organisms are known which attack mannitol, but not the stereoisomeric dulcitol, and similar relations are not uncommon.

Since a single species of bacterium may attack a very large number of different compounds, and the same compound may be decomposed in several distinct ways by different organisms, no very satisfactory classification of these fermentations can be effected, and they are best grouped according to the most characteristic of the products.

They will be briefly summarised here under the following heads :—

(*a*) **The true lactic fermentation.** In this decomposition, lactic acid is almost the sole product, the change proceeding practically in accordance with the equation :

$$C_6H_{12}O_6=2C_3H_6O_3$$

The spontaneous souring and clotting of milk have long been known to be due to the production of lactic acid, which causes the precipitation of the caseinogen. The process was at first ascribed to the action of the caseinogen itself, which was regarded as an enzyme (Boutron ; Charlard and Fremy). The souring of milk, even after it had been heated and protected from the access of air-borne germs (due to the presence of sporing bacilli), played a part of some importance in the history of the development of the theory of fermentation, and was cited by the supporters of Liebig's view, that fermentation was not due to living organisms (Gerhardt). The existence of a lactic acid producing organism was first definitely established by Pasteur (Compt. rend. 1857, 45, 813 ; 1858, 47, 224 ; Ann. Chim. Phys. 1858, [3] 52, 404), and was confirmed by Lister, in 1877, who succeeded in preparing a pure culture of an organism capable of souring milk by diluting soured milk to such an extent that a drop only contained a single organism, adding a single drop of this to sterile milk, and repeating the process several times. Since then the question has been the subject of an enormous number of investigations on account of its technical importance (*see* Lafar, Technische Mykologie, vol. 2 ; Henneberg, Gärungsbakteriologisches Praktikum, Berlin, 1909 ; Orla-Jensen, The Lactic Acid Bacteria, Copenhagen, 1919), and only a few of the most interesting results can be mentioned here.

It has been found that all liquids containing saccharine matter are liable to become sour, owing to the production of lactic acid, when they are exposed to the air. The organisms capable of producing this change are extremely numerous, and the nature of the flora developed in any particular case depends on the kind of sugar present and the character of the nitrogenous nutriment available. Thus the lactic acid organism of milk is capable of fermenting milk sugar, whilst that of beer cannot attack this substance. The chief lactic acid organisms have been isolated from milk, beer, distiller's mash, baker's yeast, dough, sauerkraut, and similar materials. They are all non-motile, and do not form spores.

Lactic acid is manufactured by the action of a bacillus on various saccharine solutions prepared from barley, maize, potatoes, &c., the starch being first hydrolysed by acid or malt, and the fermentation carried on in the presence of chalk. The organism chiefly employed for this purpose is the *B. Delbrücki* (Leichmann) identical with the *B. longissimus* (Lafar), which forms long cells (3–7μ) and grows well at 46°–47° in unhopped wort, distiller's mash, and yeast water, but not in milk or beer. It converts glucose, cane sugar, and maltose into lactic acid, and produces neither volatile acids nor alcohol. This bacillus also occurs in the unsterilised mash employed by distillers, where it is allowed to grow in order to render the liquid sufficiently acid to prevent subsequent infection by harmful bacteria during the fermentation by yeast.

A second important organism of this class is the *Saccharobacillus pastorianus* (van Laer), which frequently invades beer wort and renders the beer sour. A closely allied variety is employed in the manufacture of the Berlin white beer to impart a certain desired degree of acidity. This organism, however, produces small amounts of alcohol, acetic acid, and formic acid. It forms long cells often united to tangled threads.

The souring of milk is a very complex phenomenon, in which many bacteria belonging to different types take part, the predominant organism varying with the temperature at which the milk is preserved. The most commonly occurring organism appears to be the *Streptococcus lacticus* (Kruse), formerly known as *Bact. Güntheri* (Lehmann and Neumann), *B. lactis acidi* (Kruse), *B. acidi paralactici* (Kozai). This organism, of which there appear to be many races or varieties, forms round or oval cells, grows very feebly on nutrient gelatin, and is positive to Gram's staining reaction. It converts glucose almost completely into *d*-lactic acid, traces of volatile acids being also formed. Thus Weigmann (Jahrsb. Molk. Kiel, 1890–91, 25 ; 1891–92, 24), and Leichmann (Milchzeit. 1896, 25, 67) have found that in milk the lactic acid produced amounts to 89–98 p.c. of that calculated for the complete conversion of the milk sugar fermented into this substance.

Another organism, which has attained a certain degree of notoriety from its use for the preparation of sour milk as an article of diet, was found by Massol in Yoghurt, a sour milk used as food in Bulgaria. It is known as *B. bulgaricus* (Grigoroff), and forms long cells which grow feebly on agar, forming tangled masses of delicate threads. Its action on milk has been very thoroughly investigated by Bertrand and Weisweiller (Ann. Inst. Pasteur, 1906, 20, 977). It has practically no action on the fat, and only hydrolyses a very small proportion of the caseinogen. On the other hand, it hydrolyses the milk sugar almost completely, and ferments the resulting galactose and glucose, forming lactic acid, containing an excess of the *d*-acid, and amounting to about 92 p.c. of the hexoses fermented, about 2 p.c. each of acetic and succinic acids, traces of formic acid, and no alcohol.

The *B. acidi lactici* of Hueppe, which was at one time thought to be the chief organism concerned in the souring of milk, is not of such common occurrence as was formerly believed, and is more closely related to the following group of organisms than to the true lactic acid bacilli

(*b*) **The modified lactic fermentation,** in which lactic acid is always accompanied by a considerable proportion of other substances.

Under this head may be classed, along with others, the changes produced in carbohydrates and alcohols by the very varied and complex group of intestinal bacteria, of which *B. coli communis*, *B. typhi*, &c., are well-known representatives. This group of organisms has received a very large amount of attention from bacteriologists for several reasons. In the first place, the group includes a large number of pathogenic organisms, the detection of which is of the utmost importance. In the second place, owing to the universal and abundant occurrence of *B. coli communis* and allied organisms in the intestine, from which they pass into sewage, the presence of these organisms in water intended for consumption is regarded as a sign of pollution by sewage, and the examination for the presence of such organisms is part of the routine of a bacteriological examination of water. For these reasons, the chemical bacteriology of this group has been closely studied, especially on its qualitative side. These organisms possess the common characteristic of growing well at 37°-40°, aërobically in presence of bile salts (the sodium salts of taurocholic and glycocholic acids), and are thus differentiated from a great number of the commoner organisms of air, water, and soil, the growth of which is inhibited by these salts. In addition to this, they decompose glucose with production of acid, or acid and gas. The further chemical differentiation of these organisms depends on their behaviour to the various simple sugars and alcohols, such as the pentoses, methylpentoses, glycerol, pentitols, hexoses, and hexitols and to the complex saccharides and glucosides, to which reference has already been made.

They are all non-sporing bacilli, which either do not liquefy gelatin at all or do so very slowly, are facultative anaërobes, and are negative to Gram's staining test.

They can be distinguished independently of their chemical action by their physiological effects, notably by the agglutination test of Widal. This depends on the fact that each species, and even variety, of organism, when injected into a living animal, gives rise, in the blood serum of that animal, to a substance usually highly specific, termed an agglutinine, which is able to cause clumping and aggregation of the living bacteria when added even in very dilute solution (1 in 10,000–100,000) to a suspension of the organisms. This method affords a very valuable check on the chemical reactions, and its use has shown that in the main these reactions are reliable as a means of identification, although very considerable variations can undoubtedly be produced in the chemical reaction by artificial means, and very probably occasionally occur in nature.

Organism	Glucose	Lactose	Cane sugar	Mannitol	Dulcitol	Arabinose	Indole	V. & P.
B. lactis aërogenes (Esch.) . .	AG	AG	AG	AG	—	AG	—	+
B. acidi lactici (Hueppe) . . .	AG	AG	—	AG	—	AG	+	—
B. coli communis (Esch.) . .	AG	AG	—	AG	AG	AG	+	—
B. Neapolitanus (Emmerich) .	AG	AG	AG	AG	AG	AG	+	—
B. coscoroba (Tretrop)	AG	AG	AG	AG	—	AG	+	—
B. enteritidis (Gartner)	AG	—	—	AG	AG	AG	—	—
B. cloacæ (Jordan) .	AG	AG	AG	AG	—	AG	—	+
B. typhi (Eberth) .	A	—	—	A	—	—	—	—
B. dysenteriæ (Shiga)	A	—	—	—	—	—	—	—
B. pyogenes fœtidus (Passet) . . .	A	A	A	A	A	A	+	—

The above table shows the qualitative reactions of a few of the best-defined of these organisms; AG meaning acid and gas; A, acid only; and – no change. For the sake of completeness, the production of indole from proteins (*see Putrefaction*) is included, as well as Voges and Proskauer's test for the production of acetylmethylcarbinol (a pink colour and green fluorescence when caustic soda is added to a cultivation of the organism in glucose broth), as these are, at present, considered to be valuable tests.

The nature of the action of certain of these organisms on the carbohydrates and higher alcohols has been examined by many authors from various points of view, particularly as regards the nature of the lactic acid formed under various conditions (Péré, Ann. Inst.

Product	*B. coscoroba*						*B. typhi*	
	Glucose		Fructose		Mannitol		Glucose	
	Per cent.	C atoms	Per cent.	C atoms	Per cent.	C atoms	Per cent.	C atoms
Lactic acid . .	31·90	1·01	48·20	2·89	18·600	1·13	49·5	2·96
Succinic acid .	5·20	0·32	6·10	0·37	8·900	0·55	trace	trace
Acetic acid . .	18·84	1·13	16·10	0·97	9·500	0·58	12·7	0·76
Alcohol . .	12·85	1·01	11·50	0·90	28·100	2·22	9·1	0·70
Formic acid .	—	—	trace	trace	3·000	—	17·7	0·69
Carbon dioxide .	18·09	0·74	13·07	0·53	28·440	1·28	—	—
Hydrogen . .	0·01	—	—	—	0·015	—	—	—

Pasteur, 1893, 7, 737; 1898, 12, 63), the nature of the gas evolved (Theobald Smith, Cent. Bakt. Par. 1895, 18, 1; *see* Keyes, J. Medical Research, 1909, 21, 69, where the literature is quoted), and the quantitative relations of the various products (Harden, Chem. Soc. Trans. 1901, 612; J. Hygiene, 1905, 5, 488). The following are the results obtained by Harden for the action of an organism of the *B. coli* group on glucose, fructose, and mannitol, and for *B. typhosus* on glucose. The coli-like organism employed in these experiments fermented cane sugar and not dulcitol, and would therefore now be regarded as *B. coscoroba*. The products are expressed in percentages of the sugar fermented and also in terms of the number of carbon atoms of the sugar molecule represented by the product. The cultivations were all carried out in an atmosphere of nitrogen, to avoid atmospheric oxidation, and in presence of chalk to neutralise the acid produced, and thus to obtain a more complete utilisation of the sugar present. The carbon dioxide evolved by the action of the acid on the chalk has, in every case, been subtracted. The products in all cases were qualitatively the same.

The characteristics of the fermentation of glucose by this coli-like organism are that the lactic acid forms less than half of the total products, that alcohol and acetic acid are produced in almost molecular proportions, and that the ratio of hydrogen to carbon dioxide by volume is almost 1. *B. typhi* produces a similar change, with the exception that no gas is formed but an equivalent amount of formic acid is produced. Since *B. coli* and the allied *B. coscoroba* have the power of decomposing formates with the production of equal volumes of carbon dioxide and hydrogen, this would indicate that most probably formate is produced in all cases, but decomposed by *B. coli* and its allies, and left untouched by *B. typhi*. This is confirmed by the fact that small quantities of formic acid are often produced by the gas-forming organisms, and are increased when the cultivation is carried out under pressure.

The production of acetic acid and alcohol from glucose in approximately molecular proportions is characteristic of a large number of the organisms of this group, *B. coli communis*, *B. acidi lactici*, *B. coscoroba*, *B. Neapolitanus*, and *B. typhi*, all presenting this peculiarity (Harden).

The case of mannitol is interesting, as the effect of the change in constitution from glucose to mannitol is that the production of alcohol and carbon dioxide is almost doubled, whilst that of acetic and lactic acids is greatly diminished. Other types of intestinal organisms, for example, the various types of dysentery bacilli, which are much more restricted in their power of fermentation, produce somewhat similar effects on glucose, but in some cases much more lactic acid is produced, whilst alcohol and acetic acid are formed in a different ratio. Such types of fermentation appear to be intermediate between the true lactic fermentation and that just described.

Some light has been thrown on the mechanism of this type of fermentation by the observation that when *B. coli communis* is cultivated on nutrient agar in presence of sodium chloroacetate, a strain is obtained, probably by selection, which no longer produces gas in glucose-peptone-water (Penfold, Proc. Roy. Soc. Med. 1911, 97). Quantitative examination of the products formed by such an organism (Harden and Penfold, Proc. Roy. Soc. 1912, B, 85, 415; Grey, *ibid.* 1914, B, 87, 461) shows that formic acid is still produced from glucose and mannitol, but is not decomposed. At the same time, the amount of lactic acid produced from glucose is considerably increased at the expense of the alcohol and acetic and formic acids, whereas in the case of mannitol there is no change in this respect. It seems probable, therefore, that an intermediate product is first formed, from which lactic acid, on the one hand, and alcohol, together with acetic, formic, and probably succinic acids, on the other, are produced by the aid of two independent enzymes (Grey). The production of the intermediate compound from mannitol probably involves a special enzyme, but after this stage the remainder of the change is in all probability carried on by the same enzymes as are operative in the decomposition of glucose. As regards the formation of formic acid and alcohol and acetic and succinic acid, it is possible that formic acid and acetaldehyde in molecular proportions are the primary products (*see* Grey, Bio-Chem. J. 1913, 7, 359), but it is also possible that formic acid is produced independently of the aldehyde, and that the acetaldehyde is then partly reduced to alcohol and partly converted into an equimolecular mixture of alcohol and acetic acid, the reduction to alcohol being much greater with mannitol than with glucose. Succinic acid is also probably derived from acetaldehyde.

The occurrence of acetaldehyde as an intermediate product in this and various other types of bacterial fermentation has been demonstrated by Neuberg and Nord (Biochem. Zeitsch. 1919, 96, 133) by the use of the "fixation" method. When the fermentation is carried out in presence of sodium sulphite a considerable amount of acetaldehyde is fixed and can be isolated from the reaction products.

Corroborative evidence of this general scheme has been afforded by the further experiments of Grey (Proc. Roy. Soc. B, 1919, 90, 75, 92; 1920, 91, 294; 1921, 92, 135), who worked with an emulsion of bacteria in a solution of glucose, and estimated the amount of change at very short intervals. It was thus found that during the first period after the introduction of the bacteria a very large proportion of them died, and that the chief products formed at this stage were alcohol and acetic, formic and succinic acids. Growth then commenced, and a large proportion of the sugar was converted into a non-reducing carbohydrate. This period was followed by the almost exclusive formation of lactic acid and the disappearance of this carbohydrate.

Production of butylene glycol. Several species of intestinal bacteria differ in a very marked manner from the foregoing types, inasmuch as they produce large quantities of $\beta\gamma$-butylene glycol $CH_3{\cdot}CH(OH){\cdot}CH(OH){\cdot}CH_3$, along with small quantities of the corresponding ketoalcohol, acetylmethylcarbinol

$$CH_3{\cdot}CO{\cdot}CH(OH){\cdot}CH_3$$

This latter substance, in presence of oxygen and alkali, gives a characteristic colour reaction with proteins, known as Voges and Proskauer's reaction. The following quantitative results have been obtained with *B. lactis aërogenes* (Escherich) and similar ones are given by *B. cloacæ* (Jordan). (Harden and Walpole, Proc. Roy. Soc. 1906, B, 77, 421; Walpole, *ibid.* 1911, B, 83, 272; Thompson, *ibid.* 1912, B, 84, 500; Harden and Norris, *ibid.* 1912, B, 84, 492):—

—	Glucose		Mannitol	
	P.c.	C atms.	P.c.	C atms.
Alcohol	18·2	1·43	32·5	2·57
Acetic acid	8·6	0·52	2·1	0·12
Lactic acid	9·1	0·55	8·6	0·52
Succinic acid	4·5	0·27	2·8	0·17
Formic acid	1·7	1·21	1·6	1·53
Carbon dioxide	35·2		35·5	
Hydrogen	0·01	—	—	—
Butyleneglycol (by dif.)	(22·7)	1·72	(16·9)	1·19
Vol. ratio of H_2/CO_2	0·52	—	0·79	—

This type of fermentation, therefore, is characterised alike by the large production of alcohol and the formation of butylene glycol. As in the case of the coli-like organisms, the alcohol produced from mannitol is approximately twice as much as from glucose. The ratio of H_2/CO_2 is also much lower than is observed with the coli-like organisms.

Butylene glycol may be regarded as a reduction product of acetaldehyde

$$2CH_3{\cdot}CHO = CH_3{\cdot}CH(OH){\cdot}CH(OH){\cdot}CH_3$$

and is actually formed from acetaldehyde by *B. lactis aerogenes* (Harden and Norris, Proc. Roy. Soc. 1912, B, 84, 492). Its production, therefore, falls readily into Grey's scheme of fermentation given above.

Many bacilli not of intestinal origin also give rise to similar products. Thus, Tate (Chem. Soc. Trans. 1893, 1263) found that an organism derived from ripe pears fermented glucose and mannitol to alcohol, acetic, formic, succinic, and *l*-lactic acids, and made the interesting observation that rhamnose, a methylpentose

$$CH_3{\cdot}CH(OH){\cdot}CH(OH){\cdot}CH(OH){\cdot}CH(OH){\cdot}CHO$$

was decomposed by the same organism, but yielded no alcohol or formic acid, the products consisting of acetic, succinic, and *dl*-lactic acids. In no case did the sum of the products obtained by Tate approach the weight of the material fermented, the discrepancy being from 20–60 p.c. Again, the pneumobacillus of Friedländer (*B. pneumoniæ*) was found by Grimbert (J. Pharm. Chem. 1895, [6] 2, 529) to yield 36–58 p.c. of *l*-lactic acid from glucose and mannitol, along with alcohol, and acetic acid; whilst Frankland, Frew, and Stanley (Chem. Soc. Trans. 1891, 253) obtained no lactic acid, but only alcohol, acetic, succinic, and formic acids and a large volume of carbon dioxide and hydrogen, the products from mannitol being in the ratio

$$9C_2H_6O : 4C_2H_4O_2 : 10CO_2 : 8H_2$$

whilst relatively less alcohol was formed from glucose. The discrepancy between these results probably points to imperfect identification of the organism on the part of one or other of these observers or else to a wide difference in chemical action between different varieties of the same organism.

(*c*) **The butyric fermentation.** Normal butyric acid and normal butyl alcohol are formed from carbohydrates, higher alcohols, glycerol, lactic acid, and other compounds by the action of many bacteria, and, in addition to this, organisms are also known which produce butyric acid from proteins.

The butyric fermentation, well known as a means of preparing butyric acid by the inoculation of a glucose solution with decaying cheese, was first ascribed to a specific organism by Pasteur (1861). He named this organism the *Vibrion butyrique*, and made the highly important observation that its motility was destroyed by the presence of oxygen, a phenomenon which led to the recognition of the existence of anaërobic organisms and to Pasteur's celebrated theory, 'La fermentation est la vie sans air.' The subsequent researches of Prazmowski, Gruber, Botkin, Beyerinck, Flügge, and many others, added to the *Vibrion butyrique* of Pasteur as producers of butyric acid a large number of species of varying forms and properties. The bacteria which produce butyric acid from carbohydrates are characterised by an extreme tendency to variety and multiplicity of form. Moreover, they all form spores, many of which are extremely resistant to heat, and these facts, coupled with the difficulty of isolating pure cultures under anaërobic conditions, have given rise to the greatest confusion in the literature of the subject, and to considerable difficulty in the identification of species.

The study of the anaërobic bacteria obtained from wounds, carried out with an improved technique, has, however, resulted in a considerable advance in our knowledge of this group of organisms (*see* Report to Medical Research Committee, McIntosh, 1917, and Reports of the Committee upon Anaërobic Bacteria and Infections, 1918, 1919, where the literature is quoted), although the chemical changes produced by them have not yet been thoroughly worked out.

These organisms are best classified according to their morphology and chemical action, as shown in the following table (Report of Anaërobe Comm. 1919, 47):—

(*a*) Central or subterminal spore.

A. Both proteolytic and saccharolytic properties.

1. Proteolytic properties predominating. (Coagulated serum and gelatin are liquefied.)

B. sporogenes; *B. parasporogenes*; *B. hisolyticus*; *B. aerofetidus*; *B. bifermentans.*

2. Saccharolytic properties predominating. (Serum not liquefied. Gelatin liquefied.)

B. Welchii; *Vibrion septique*; *B. chauvoei*; *B. œdematiens*; *B. botulinus.*

C. Saccharolytic but no proteolytic properties. (Neither serum nor gelatin liquefied.)

B. fallax; *B. butyricus*; *B. multifermentans tenalbus.*

(*b*) Oval terminal spore.

C. Saccharolytic but no proteolytic properties.

B. tertius.

D. Neither saccharolytic nor proteolytic properties.

B. cochlearius.

(*c*) Spherical terminal spore.

B. Slight proteolytic but no saccharolytic properties. (Serum not liquefied. Gelatin liquefied.)

B. tetani.

C. Saccharolytic but no proteolytic properties.

B. tetanomorphus; *B. sphenoides.*

The proteolytic group ((*a*) A. 1) comprises a number of different organisms, the chief chemical action of some of which is the decomposition of proteins and amino-acids (*B. histolyticus*; *see* under *Putrefaction*). *B. sporogenes* (Metchnikoff) occurs in animal excreta and in soil. It is a large motile bacillus, which readily forms spores. These are very resistant to heat, and are not destroyed when the liquid in which they are suspended is boiled for many minutes. It decomposes glucose in a similar manner to *B. Welchii* (*see below*), but from milk it produces valeric and caproic, in addition to butyric and acetic, acids (Wolf and Telfer, Biochem. J. 1917, 11, 197).

The non-proteolytic group ((*a*) A. 2) includes several organisms capable of setting up pathogenic conditions in man and other animals, more particularly gas-gangrene. *B. Welchii*, also known as *B. aerogenes capsulatus* (Welch), *B. perfringens* (Veillon and Zuber), and *B. enteritidis sporogenes* (Klein), occurs in soil, and is also regularly found in cow-dung, from which it passes into milk. It is a frequent infection of wounds, and is pathogenic to guinea-pigs. It ferments the sugars and starch, but not mannitol or cellulose, and attacks glycerol. Both from milk and glucose large quantities of butyric and acetic acid are formed, along with carbon dioxide and hydrogen and a non-volatile acid (presumably lactic acid) (Wolf and Telfer, Biochem. J. 1917, 11, 197). This organism, which is one of those responsible for the production of gas gangrene in cases of wound infection, when grown under suitable conditions produces a toxin, from which a potent antitoxin can be prepared (Bull).

Among other organisms in this group are the *Vibrion septique* (*Pasteur and Joubert*) or bacillus of malignant oedema, which is largely responsible for the gas-gangrene resulting from infected wounds; *B. chauvoei*, the bacillus of black-quarter (Rauschbrand) an impure culture of which was described by Grassberger and Schattenfroh as the non-motile butyric acid bacillus, *B. botulinus*, which has been found in certain cases of food-poisoning and *B. oedematiens*. None of these has yet been carefully examined from the chemical point of view.

Another important anaërobe (Group (*a*) C) is *Bacillus butyricus*. This comprises Pasteur's original *Vibrion butyrique* and the organisms previously known as *B. amylobacter* (Grüber), the motile butyric acid bacillus of Grassberger and Schattenfroh, *Clostridium butyricum* (Prazmouski), *Granulobacter saccharobutyricus* (Beyerinck), *B. saccharobutyricus* (Klecki). It is found in soil, water, and cheese, but less frequently in milk, and is typically a short bacillus with rounded to almost pointed extremities. It ferments glucose, saccharose, lactose, starch, and glycerol with production of butyric and lactic acid and evolution of carbon dioxide and hydrogen (Grassberger and Schattenfroh, Arch. Hyg. 1902, 42, 219).

B. tetani (Group (*c*) B) is highly pathogenic to animals, producing tetanic convulsions (lockjaw) and death. Several distinct types of this organism occur, which can only be distinguished by their serological reactions. It forms a powerful toxin in broth, which is used for the preparation of an antitoxin. It does not ferment carbohydrates, and has a slight action on meat, without producing putrefaction.

In some detached instances examinations of chemical products have been made with cultures of doubtful purity. Thus the *B. butylicus* of Fitz (Ber. 1878, 11, 49), obtained from hay infusion, gave the following results with glycerol, mannitol, and invert sugar:—

	Glycerol p.c.	Mannitol p.c.	Invert sugar p.c.
n-Butyl alcohol .	8·1	10·2	0·5
n-Butyric acid .	17·4	35·4	42·5
Lactic acid .	1·7	0·4	0·3
Succinic acid .	—	0·01	trace
Trimethylene glycol	3·4	—	—

The fermentation of glycerol by this organism has been recommended by Fitz, and subsequently by Freund, as a convenient method for the preparation of *n*-butyl alcohol and of trimethylene-glycol.

Buchner and Meisenheimer (Ber. 1908, 41, 1410), also working with the *B. butylicus* of Fitz, obtained analogous results, as did also Perdrix (Ann. Inst. Pasteur, 1895, 5, 286) with the *B. amylozyma* (Perdrix).

An organism termed *B. amylobacter pectinovorum*, the exact position of which in the classification is not clear, has been employed for the commercial production of acetone and *n*-butyl alcohol from maize (Fernbach and Strange, 1912, Eng. Pat. 21073; Weizmann, 1915, Eng. Pat. 4845). The chemical side of the process has been described by Reilly and his colleagues (Biochem. J. 1920, 14, 229), and by Speakman (J. Biol. Chem. 1920, 41, 319; 43, 401), and the necessary plant by Speakman (J. Soc. Chem. Ind. 1919, 38, 155 T). A 6·5 p.c. mash of maize is employed and the organism produces from the maize 7 p.c. of acetone and 16 p.c. of butyl alcohol, together with small amounts of acetic and butyric acids and a non-volatile acid. A large volume of gas, consisting of carbon dioxide and hydrogen, is evolved, 100 lbs. of maize yielding 341 cubic feet or 40·7 p.c. of CO_2, and 209 cubic feet or 1·1 p.c. of H_2. The acetone and butyl alcohol are distilled off and purified by fractional distillation. In the presence of calcium carbonate very little acetone and butyl alcohol are formed, the products consisting of acetic acid, butyric acid, and gas. The yield of acetone is greatly increased by the addition of acetic acid and that of butyl alcohol by butyric acid, and it seems probable that in the normal fermentation acetic and butyric acids are intermediate products.

The occurrence of acetone among the products of carbohydrate fermentation had previously frequently been recorded (*see* Schardinger, Centr. Bakt. Par. 1905, ii. 14, 772). A considerable yield was obtained by Schardinger by the action of the spore-forming *B. macerans* on potatoes and plums, alcohol and acetic and formic acid being also produced, but no lactic or butyric acid.

The production of butyric acid and butyl alcohol from glycerol and lactic acid by means of the butyric bacillus is of great theoretical importance, since it involves a synthesis from the primary products of the rupture of the carbon chain. It has been suggested by many observers that one of these is acetaldehyde from which the butyric acid and butyl alcohol could readily be formed by an aldol condensation, followed by reduction or a combined oxidation and reduction:

$$2CH_3{\cdot}CHO = CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CHO$$

$$CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CHO + 4H = CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2(OH) + H_2O$$

That lactic acid is not necessarily an intermediate product in the butyric fermentation, as suggested by Buchner and Meisenheimer, is shown by the fact that certain organisms will not ferment lactic acid in this way, although they produce butyric acid from sugars.

Neuberg and Arinstein (Biochem. Zeitsch. 1921, 117, 269) have applied the sulphite 'fixation' method to the fermentation of sugar produced by *B. butylicus fitzianus*, and have found that autaldehyde is produced. Neither autaldehyde itself, however, aldol nor pyruvic acid yielded butyric acid when treated with the organism, whereas the aldol of pyruvic acid

$$CH_3{\cdot}C(OH)(COOH){\cdot}CH_2{\cdot}CO{\cdot}COOH$$

gave a good yield, and they therefore consider that this substance is produced as an intermediate product.

The detection of anaërobic butyric acid bacteria in milk (Klein's *B. enteritidis sporogenes*) forms part of the routine examination of milk for fæcal contamination, and is carried out by heating the milk to 80° for 10 minutes, to destroy all vegetative forms and leave only the resistant spores, and incubating measured quantities of the liquid anaërobically. A characteristic separation of the caseinogen in flocculi, accompanied by a smell of butyric acid and the development of Gram-positive rods pathogenic to guinea-pigs, indicates the presence of the bacillus.

(*d*) **The fermentation of cellulose and bacterial production of methane.** The bacterial fermentation of cellulose takes place on a vast scale in the soil, especially in marshy places, and appears to be one of the chief processes by which the cellulose of plant remains is resolved into simpler products. It is to this decomposition that is due the evolution of an inflammable hydrocarbon from marshes, which was first recognised by Volta in 1776. A similar decomposition occurs in the stomachs of graminivorous animals (Tappeiner) and in heaps of manure, wool, refuse, &c. The fact that cellulose was capable of undergoing fermentation was first observed by Mitscherlich in 1850, who ascribed the gradual disappearance of the cell walls of potatoes left in water for several days to the action of bacteria. The power of destroying cellulose was subsequently (erroneously) attributed by van Tieghem (Compt. rend. 1879, 88, 205; 89, 25, 1102) to the *B. amylobacter* (Gruber), on the ground of the destructive action of this bacillus on many vegetable tissues. A considerable amount of information as to the chemical nature of the process of cellulose fermentation was afforded by the researches of Popoff (Arch. Phys. 1875, 10, 113), Tappeiner (Ber. 1881, 2375; 1882, 999; 1883, 1734; 1884, 142, 262, 587), and Hoppe-Seyler (Zeitsch. physiol. Chem. 1886, 10, 201, 401; Ber. 1883, 16, 122). Popoff and Hoppe-Seyler worked with sewer mud, and found that it contained organisms capable of decomposing Swedish filter paper, and producing from it carbon dioxide, methane, and sometimes hydrogen. Hoppe-Seyler, indeed, was able to bring about the conversion of 25·8 grams of pure filter paper into marsh gas and carbon dioxide in 4 years at room temperature, no other products being formed. Tappeiner paid attention chiefly to the extremely interesting problem of the decomposition of cellulose in the animal intestine, which had previously been ascribed to the action of a soluble enzyme (Hofmeister). He showed that a large part, if not the whole, of this decomposition, which in ruminants may amount to as much as 75 p.c. of the cellulose ingested, is bacterial and is accompanied by the evolution of large volumes of carbon dioxide, marsh gas, and sometimes hydrogen. He was moreover able to show that two types of cellulose fermentation existed, one of which was characterised by the production of methane, the other by that of hydrogen, methane being formed when the nutrient medium contained beef extract, hydrogen when only salts of known composition were used. In both cases carbon dioxide was evolved, and aldehyde and large quantities of acetic and butyric acids were produced. No advance had, up to this time, been made in the determination of the specific bacteria to which the destruction of cellulose was due, this function being generally ascribed to *B. amylobacter*, although van Senus (Koch's Jahrb. 1890, 1, 136) considered that the presence of a second organism was necessary. Much light has been thrown on the whole subject by the long-continued researches of Omelianski (Centr. Bakt. Par. Abt. ii. 1902, 8, 193; 1904, 11, 369; 12, 33; 1906, 15, 673; article in Lafar, Technische Mykologie, 1904, iii. 245). Omelianski has found that the fermentation of cellulose is produced by anaërobic sporing bacteria, and agrees with Tappeiner in recognising the methane and hydrogen types of fermentation. These are brought about by different organisms, which can be separated if advantage be taken of the fact that when a mixed culture of the spores of both varieties, such as occurs naturally in sewer mud or manure, is inoculated into the nutrient solution described below, and cultivated anaërobically, the bacteria of the methane fermentation are the first to grow. Accordingly, when such a mixed culture is allowed to develop and is then heated to 75° for 15 minutes, the vegetative forms of the methane bacteria are killed, and a succession of inoculations and heatings suffices to remove the whole of these, and leaves a culture which produces a pure hydrogen fermentation. On the other hand, direct inoculation without heating leads to the elimination of the undeveloped spores of the hydrogen organism and the production of a pure methane fermentation. It has not so far been found possible to obtain cultures of either form on solid media, and Omelianski relies on the strongly selective character of his medium and the microscopic appearance of his cultures as the only guarantees of their purity. The medium found suitable consists of potassium phosphate, 1 gram; magnesium sulphate, 0·5 gram; ammonium sulphate or phosphate, 1 gram; sodium chloride, trace; distilled water, 1 litre. To 300 c.c. of this, 3–4 grams of Swedish filter paper and 5–6 grams of chalk are added, and the whole inoculated. The fermentation only begins after at least a week's incubation, and proceeds slowly for many months. Spots slowly appear on the paper, and these gradually become perforations, and the paper breaks up into fragments and finally disappears. The decomposing fragments are found to be densely covered with bacteria, which are very slender, isolated rods, those of the methane fermentation being somewhat the thinner of the two species. They gradually produce at one end a round spore, three times the diameter of the rod (drumstick form). The bacilli can be stained by the ordinary aniline dyes, and do not give a blue coloration with iodine.

In the absence of any isolation of the bacteria on solid media or cultivation from a single spore, it must still be regarded as doubtful whether either of these organisms has yet been obtained in pure culture.

The products of decomposition of cellulose were examined quantitatively by Omelianski, and found to be as follows:—

	Hydrogen fermentation	Methane fermentation
	p.c.	p.c.
Carbon dioxide . . .	29·1	43·2
Hydrogen . . .	0·4	—
Methane . . .	—	6·8
Acetic acid . .	35·9	43·6
Butyric acid . .	31·0	7·1
	96·4	100·7

Pringsheim (Centr. Bakt. Par. 1913, ii. 38, 513) has found that the fermentation of cellulose can be brought about anaërobically by many thermophilic bacteria, which have the remarkable property of growing best at 55°–60°C., temperatures at which most bacteria are killed. The products in this case are hydrogen and carbon dioxide, along with acetic and formic, but no butyric, acid. Cellulose is also decomposed by certain denitrifying organisms. The same author has shown that in all processes of the bacterial fermentation of cellulose a preliminary hydrolysis occurs, brought about by the cellulase of the organism, with formation of the disaccharide cellobiose, which is then further hydrolysed and the products fermented (Zeitsch. physiol. Chem. 1912, 78, 266). Cellulose is also attacked and disintegrated by various aërobic organisms and by certain moulds (*see* McBeth, Soil Science, 1916, 1, 437), but little is known as to their mode of action. The materials containing the cellulose-fermenting bacteria also contain organisms which are capable of producing methane from a great variety of substances, among which are acetates (Hoppe-Seyler), butyrates (Mazé), and generally the fatty acids containing an even number of carbon atoms in the molecule (Söhngen); alcohol and gum arabic (Omelianski), and, according to Tappeiner, various albumins and protein derivatives. Omelianski also obtained from decaying wood organisms which produced methane fermentation with egg albumin, glue, gelatin, wool, and peptone. Fermentations of this kind undoubtedly play a large part in the destruction of animal and vegetable remains and are of great technical importance in the decomposition of sewage in the septic tank and in the fermentation of manure. An interesting consequence of their constant occurrence in nature is the presence of methane in the air, as much as 11·3 c.c. per 100 litres having been found by Gautier in the air of wooded rural districts, where the decomposition of vegetable matter in the soil is probably very considerable.

Other types of fermentation by decomposition. Fermentation of the hydroxy-acids and glycerol. Among the numerous other types of fermentation involving the rupture of the carbon chain of non-nitrogenous compounds, only a few can be mentioned here.

i. The *B. ethaceticus* (F.) was isolated in 1890 from sheep dung by Frankland, who carefully examined its action on a number of different substances. This organism does not appear to have been identical with any of the more recently described intestinal bacteria. It fermented glucose, mannitol, arabinose, and glycerol, forming mainly acetic acid, alcohol, formic acid, and a mixture of equal volumes of carbon dioxide and hydrogen. No lactic acid was produced, but from glucose and arabinose a fixed acid of unknown composition was probably formed (Frankland and Fox, Proc. Roy. Soc. 1890, 46, 345; Frankland and Frew, Chem. Soc. Trans. 1891, 81; Frankland and Lumsden, *ibid.* 1892, 432; Frankland and MacGregor, *ibid.* 1892, 737). This organism had the interesting property of fermenting a solution of calcium *dl*-glycerate asymmetrically, only decomposing the *l*-acid and leaving unattacked the pure *d*-acid, which was first isolated in this way. The decomposition is represented by the equation:

$$5C_3H_6O_4 = C_2H_6O + 4C_2H_4O_2 + 5CO_2 + 3H_2 + H_2O$$

This organism, after repeated cultivation in calcium glycerate, however, acquired the power of slowly fermenting the *d*-acid.

ii. *Glycerol* undergoes fermentation by many organisms, and in some cases yields butyric acid, as has already been described.

A more usual change is its decomposition mainly into alcohol and formic acid or carbon dioxide and hydrogen:

$$C_3H_8O_3 = C_2H_6O + CO_2 + H_2$$

This was observed by Fitz with an organism known as *B. ethylicus* or *fitzianus*, and this is also the type of decomposition produced by *B. coli communis* (Harden).

iii. *The hydroxy-acids*, such as lactic acid, malic acid, and citric acid, are readily decomposed by many organisms. Thus lactic acid, in addition to undergoing butyric fermentation, is converted by a mixed fermentation (Strecker, 1854, Fitz) into acetic acid, propionic acid, and carbon dioxide. Malic acid yields with *B. lactis aërogenes*, carbon dioxide, acetic acid, and a large amount of succinic acid (Emmerling), similar products being formed by *B. cloacæ* (Thompson), whilst citric acid is converted by these two organisms into carbon dioxide and acetic acid.

iv. *The mannitol fermentation* is effected by an organism which occurs as an infection in wines (Gayon and Dubourg, Ann. Inst. Pasteur, 1894, 8, 108; 1901, 15, 527). It decomposes sugars into alcohol, carbon dioxide, acetic, lactic, and succinic acids, and glycerol, but with fructose yields a considerable proportion of mannitol.

3. Fermentations by Oxidation.

All aërobic organisms have the power, like the higher plants and animals, of oxidising appropriate food materials, with production of carbon dioxide and water. It is, however, frequently possible, in the case of bacteria, to isolate partially oxidised products and thus ascertain some of the stages of the process, whereas this can only rarely be accomplished with higher organisms. The production of acetic acid from alcohol by bacterial action is one of the most important cases of this kind: the conversion of ammonia into nitrous acid, and this into nitric acid, being a second.

(*a*) **The acetic fermentation of alcohol and the oxidising properties of the bacteria which produce it.** The spontaneous souring of wine, beer, and other alcoholic liquors when exposed to air has long been known and employed for the manufacture of vinegar. Pasteur, in 1864 (Mém. sur la fermentation acétique; Ann. École Norm. sup. 235, 225; J. Chem. Soc. Abstr. 1881, 128; Études sur le vinaigre, 1868), conclusively proved that the change of alcohol into acetic acid in this process was due to the 'flowers of vinegar,' an organism which, from the circumstance that it formed a film on the surface of the liquid, he termed *Mycoderma aceti*. Pasteur carefully examined this organism, cultivated it in synthetic media, and proved that it acted as a carrier of oxygen from the air to the alcohol, and that it was capable, when no more alcohol was available, of oxidising the acetic acid to carbon dioxide and water. Traces of aldehyde were observed to be produced when the vitality of the organism was impaired. The application of Neuberg's 'fixation' method (fermentation in presence of sodium sulphite) leads to a large accumulation of acetaldehyde (Neuberg and Nord, Biochem. Zeitsch. 1919, 96, 158). Since Pasteur's time a large number of organisms have been found which have a similar action on alcohol, and which include those found in vinegar breweries. These are not very clearly characterised, and only one or two of the most important can be here mentioned (*see* Henneberg, various papers in Centr. Bakt. Par. Abt. ii. 1897–98, 1905–6; and Gärungsbacteriologisches Praktikum, Berlin, 1909, 510–558). *B. aceti* (Hansen) has been studied morphologically by Cohn (Biol. d. Pflanzen, 2, 173), and biochemically by A. J. Brown (Chem. Soc. Trans. 1886, 174; 1887, 638) and Hansen. It grows on the surface of culture media, forming an easily broken film, consisting of chains of cells about 2 inches in length, and slightly contracted in the middle, so that they resemble a figure of 8. It does not form spores, and readily produces involution forms, cells of 10–15 μ in length and irregularly swollen being common. As regards the production of acetic acid from alcohol, Brown fully confirmed Pasteur's observations with *Mycoderma aceti*. The highest concentration of acetic acid that can be obtained by the use of this organism is 6·6 p.c. (Henneberg).

Brown also found that this organism converts *n*-propyl alcohol into propionic acid, and glycol into glycollic acid, but does not act on methyl alcohol or erythritol, whilst it oxidises glycerol completely. The observation that this bacillus converts glucose into gluconic acid (Boutroux, Compt. rend. 1878, 86, 605; 1880, 91, 236) was confirmed. Mannitol undergoes an extremely interesting reaction, being converted into fructose. All these reactions occur when the organism is grown on solutions of the various substances in yeast water, chalk being added to neutralise the acids formed.

As already mentioned, Buchner and Gaunt (Annalen, 1906, 349, 140) have shown that the oxidation of alcohol by this organism is due to the action of an enzyme, and can be effected by the cells after they have been killed and dehydrated by acetone.

B. xylinus (Brown) is the organism which occurs in the vinegar plant, or mother of vinegar, in which it is associated with a yeast. The mixed growth is thus capable of converting cane sugar solution into vinegar, the sugar, which is itself not attacked by the bacillus, being hydrolysed and fermented by the yeast, with production of alcohol, which is then oxidised by the bacillus. The *B. xylinus* in pure culture grows on the surface of alcoholic liquids, forming thick, tough gelatinous membranes, which sometimes on wine attain a thickness of as much as a foot. This is due to the formation of a transparent film in which the short, rod-like bacilli are embedded. This film contains a large proportion (35–63 p.c. of its dry weight) of a cellulose-like material (Brown), which, however, contains nitrogen, and is probably a glucosamine derivative (Emmerling, Ber. 1899, 32, 541). The chemical actions of this organism were found by Brown to agree in general with those of *B. aceti*. They have been more completely investigated by Bertrand (Ann. Chim. 1904, [8] 3, 181), who terms the organism the sorbose bacterium. He finds that this organism converts many polyvalent alcohols into the corresponding *a*-ketose, thus changing sorbitol into sorbose, mannitol into fructose, *i*-erythritol into erythulose $CH_2(OH)·CO·CH(OH)·CH_2OH$, *l*-arabitol $C_5H_{12}O_6$ into arabinulose $C_5H_{10}O_5$, perseitol and volemitol $C_7H_{16}O_7$, into perseulose and volemulose $C_7H_{14}O_7$. Of great interest is its action on glycerol, which it converts into dihydroxyacetone $CH_2(OH)·CO·CH_2·OH$, entirely free from the isomeric glyceraldehyde which is invariably formed by the action of ordinary oxidising agents.

This method is by far the most convenient for the preparation of dihydroxyacetone, the organism being simply grown for about 3 weeks on a 10 p.c. solution of glycerol in yeast water, and the liquid then evaporated, precipitated by alcohol, filtered and finally evaporated *in vacuô*.

On the other hand, glycol, *l*-xylitol, and *d*-dulcitol are not attacked. The action of the bacillus is confined to the oxidation of a secondary carbinol group, which is not stereochemically in the neighbourhood of a hydrogen atom (Bertrand). The aldoses are oxidised to the corresponding acid, glucose, xylose, arabinose, and galactose all behaving normally in this respect. When the acid thus produced contains a CH(OH) group capable of being attacked, according to the rule just stated, this may also be oxidised. Thus gluconic acid yields the corresponding ketonic acid, oxygluconic acid $CH_2(OH)·CO·CH(OH)·CH(OH)·CH(OH)·COOH$, which had previously been obtained by Boutroux by the aid of the *M. oblongus* (Bout.) (Compt. rend. 1886, 102, 924).

(*b*) **Nitrification.** The conversion of the nitrogen of organic matter into nitrates in the soil was familiar to chemists at a very early date, and was employed as a means of manufacturing saltpetre. From the time of Mayow onwards, it was regarded as a purely chemical action brought about by the agency of the porous soil, or, according to Liebig's characteristic view, by a ferment, *i.e.* some substance which was itself undergoing oxidation in the soil. The idea that this process was in reality of biological origin was suggested by Pasteur (1862), but first more fully developed by Schloesing and Müntz (Compt. rend. 1877, 84, 301; 1878, 86, 392; 1879, 89, 891, 1074), who found that nitrification ceased when the soil was sterilised by heat or antiseptics. The researches of Warington (Chem. Soc. Trans. 1878, 44; 1879, 429; 1884, 637; 1888, 727), carried out at Rothamsted, contributed, along with much information as to the conditions of nitrification, the fundamentally important facts that oxidation often only proceeded as far as the production of nitrite, and that the nitrogen was converted into ammonia before being nitrified. These conceptions were then further developed by Munro (Chem. Soc. Trans. 1886, 632), who came to the conclusion that the normal course of nitrification consisted in the production of ammonia followed by that of nitrites and nitrates. Up to this time (1888), all attempts to isolate the organisms by the aid of which the change was effected had failed, and it was not until this had been effected by Winogradsky (Ann. Inst. Pasteur, 1890, 4, 213; article in Lafar, Technische Mykologie, 1904, iii. 132–181), and almost simultaneously by Warington (*see* Chem. Soc. Trans. 1898, 484), that the true conditions of the process were discovered. The bacillococcus possessed of nitrifying power which was described by P. and G. Frankland (Proc. Roy. Soc. 1890, 47) was subsequently found not to be a pure culture. Winogradsky, convinced that the presence of organic matter was detrimental to the development of the organism, inoculated with earth a solution containing only 1 per mille of ammonium sulphate and of potassium phosphate, together with some solid basic magnesium carbonate, and by repeated sub-cultivations succeeded in obtaining strong nitrification in a liquid almost free from organisms capable of growing on the ordinary solid media. The principle involved is that of selective culture, only those organisms surviving which can avail themselves of the very limited supply of nourishment provided. The deposit of magnesium carbonate in such solutions was observed to be covered with gelatinous masses of the nitrifying organism, and when this was spread on gelatin, it was found that many particles produced no growth whatever, and were therefore free from all ordinary soil organisms. Some of these, when removed and placed in the culture fluid, produced active nitrification, and a growth in which no foreign organisms could be detected. It was subsequently found by Winogradsky that this organism was only capable of converting ammonia into nitrite, and that the final stage of the oxidation to nitrate was effected by a second organism, which was isolated (1891) in a similar manner, by repeated sub-culture in a selective culture medium containing sodium nitrite instead of an ammonium salt. This discovery led to the explanation of the apparently capricious action of the nitrifying organisms, which sometimes yielded nitrite and at others nitrate. It was found, in confirmation of the opinion expressed by Warington, that the development of the nitrate-producing organism was inhibited by comparatively small proportions of ammonium salts. This effect is, in fact, very remarkable, and is comparable to that of the most powerful antiseptics. In a particular case as little as 0·005 gram per litre of ammonia (as sulphate) caused a perceptible diminution in the rate of nitrification of a nitrite solution, and 0·154 gram completely inhibited it. On the other hand, nitrites may be present up to at least 10 grams per litre, and nitrates to 20 grams per litre. When, however, ammonia is added to a liquid containing a well-developed culture of the nitrate-producing organism, it causes very little change in the rate of action, even in quantities of 1·8 grams per litre, so that its harmful effect is mainly one of inhibition, exerted on the development of the organism, and not on the oxidising action of the developed organism (Winogradsky).

In agreement with these facts, it is found that when an inoculation of earth is made into solutions of ammonium salts, *nitrosification* (the production of nitrite) proceeds until nearly all the ammonia has been converted, and only then does the production of nitrate begin. The repeated addition of fresh ammonia before this second stage sets in will limit the action entirely to the production of nitrite. If, however, nitrate production is once well established, further additions of ammonia are completely converted into nitrate. Similar conditions prevail in the nitrification of sewage, which is apparently effected by the same organisms as are found in the soil (Chick, Proc. Roy. Soc. 1906, B, 77, 241).

Another remarkable feature of these organisms is their mode of carbon assimilation. Organic carbon not only cannot be assimilated by them, but actively inhibits their development in culture solutions, compounds such as glucose and peptone totally inhibiting nitrosification in concentrations of 0·2 p.c. and nitrification in concentrations of 0·25 p.c. (glucose), and 1·25 p.c. (peptone), and behaving, therefore, in this respect like powerful antiseptics. It was this property which rendered the isolation and artificial culture of these organisms so difficult. In the soil, however, these compounds are not harmful, and even aid the process of oxidation (Coleman, Centr. Bakt. Par. 1908, ii. 20, 401). The sole source of carbon for both classes of organism appears to be carbon dioxide, derived from carbonates by the nitrosifying organism, and from bicarbonates by the nitrifying organism. The energy necessary for the reduction of carbon dioxide to assimilable compounds is apparently provided by the oxidation of the ammonia or nitrite, and a fixed ratio exists between the amounts of carbon assimilated and ammonia or nitrite oxidised. Thus the nitrosifying organism oxidises 35·4 parts of nitrogen as ammonia for 1 part of carbon assimilated (Winogradsky).

The study of the morphological characteristics of the organisms of this highly important group has been greatly aided by the discovery of solid media on which cultivations can be made. Winogradsky first introduced a jelly of silica saturated with the culture fluid, and Omelianski has successfully used plates made of gypsum and 1 p.c. of magnesium carbonate, and even discs or strips of filter paper. More convenient are the agar plates introduced by Beyerinck (Cent. Bakt. Par. ii. 1896, 19, 258). The agar-water jelly is allowed to stand for about a fortnight under water. Fermentation occurs, accompanied by the decomposition of all the compounds which inhibit the growth of the nitrifying organisms. The agar is then washed, mixed with the culture medium and a little chalk, and finally sterilised.

The exact relations of the various organisms which have been isolated are still unknown. The general result is that several nitrosifying organisms have been obtained from different regions, whereas hitherto only one nitrifying organism has been found. The nitrosifying organism is termed *B. nitrosomonas* (Winog.), L and N. The forms of the West European variety are oval bacilli (1×1·2–1·8μ), which produce zooglœa in fluid media, and brown colonies on solid media; these break up after some time into motile forms. The organism from Buitenzorg in Java, on the other hand, is a minute micrococcus 0·5–0·6μ in diameter, and that from Quito a large coccus 1·5–1·7μ in diameter, which does not form zooglœa. The organism from Japan closely resembles the European variety. Hitherto only one variety of this organism has been obtained in any one district.

B. nitrobacter (Winog.), L. and N., which converts nitrites into nitrates, is a bacillus 1×0·3–0·4μ, possesses a gelatinous capsule, and never forms motile cells. It grows very slowly on agar, forming almost colourless, drop-like colonies.

(*c*) **Other oxidising effects produced by bacteria. Oxidation of sulphuretted hydrogen, ferrous oxide, hydrogen, and methane.** Very special interest attaches to the action of bacteria in bringing about the oxidation of sulphuretted hydrogen. This process is comparable with the nitrification of ammonia, inasmuch as it has the effect of converting sulphuretted hydrogen, a direct product of the putrefaction of proteins, into sulphates, from which plants are able to supply themselves with the sulphur essential for their growth.

Early observers noted the occurrence of characteristic micro-organisms in sulphur wells, and the presence of granules of sulphur within their cells (1870–1875), but it is to the researches of Winogradsky that we owe, in the main, our present knowledge of the sulphur bacteria. The oxidation of sulphuretted hydrogen is effected in two stages. The first product is free sulphur, which is deposited in the cell in the form of soft spherical granules of amorphous sulphur. In the presence of abundance of sulphuretted hydrogen, the cell becomes crowded with these particles. The second stage consists in the oxidation of this sulphur to form sulphuric acid, which neutralises the carbonates present in the soil to form sulphates. It seems probable that these organisms derive the whole of their carbon from carbon dioxide, the energy necessary for its decomposition being derived from the oxidation of the sulphuretted hydrogen. Many genera of sulphur bacteria are known, the most important being *Beggiatoa* and *Thiothrix*, which form long threads, and are regarded by some authors as intermediate between the bacteria and algæ. In addition to these, a large number of others have been described, many of which are characterised by the production of a red colouring matter known as bacteriopurpurin (Ray Lankester).

Another group of bacteria is known, the species of which bring about the oxidation of ferrous hydrogen carbonate to ferric hydroxide in chalybeate waters. These organisms, which, like the sulphur bacteria, form long threads, are also closely allied to the algæ, and belong to the genera *Crenothrix*, *Cladothrix*, *Streptothrix*, &c. They are also able to effect the oxidation of manganese salts, and the resulting oxides are apparently deposited in the gelatinous membrane of the cell (Molisch, quoted by Rullmann, Lafar, iii.).

Other groups of bacteria are able to play the part of platinum black in bringing about the oxidation of hydrogen (Lebedev, Biochem. Zeitsch. 1907, 7, 1; Lebedev and Nabokich, Centr. Bakt. Par. ii. 1906, 17, 350; Niklewski, Centr. Bakt. Par. ii. 1907, 21, 380), whilst others can effect the oxidation of marsh gas (*B. methanicus*, Söhngen, Proc. K. Akad. Wetensch. Amsterdam, 1905, 8, 327), and an organism has been described by Beyerinck (Centr. Bakt. Par. ii. 1909, 25, 30) which can bring about reaction between nitrous oxide and hydrogen, and obtain its carbon from carbon dioxide by the aid of the energy thus liberated.

4. Fermentations by Reduction and Deoxidation.

(*a*) **Reduction.** The decomposition of a molecule of a carbon compound into two or more smaller molecules, some of which are relatively more oxidised and others relatively more reduced, is, as we have seen, a common feature of many fermentations by decomposition. A typical example is afforded by the alcoholic fermentation of sugar, which results in the formation of carbon dioxide on the one hand, and alcohol on the other. The decomposition sometimes results in the production of free hydrogen, and when this occurs in the presence of reducible substances, reduction often takes place. Of this secondary character are the reduction by *B. coli communis* of nitrates to nitrites in presence of sodium formate (Pakes and Jollyman, (Chem. Soc. Trans. 1901, 459), and of aspartic acid in presence of glucose to ammonium succinate (Harden, *ibid.* 1901, 612), the reduction being effected by the hydrogen produced from the formate and glucose respectively. Many similar cases are known, especially among mixed fermentations (*see* Söhngen, Rec. trav. chim. 1910, 29, 238). In other cases the reducing action of bacteria is exercised directly upon the reducible compound, and results either in the direct removal of oxygen or the addition of hydrogen. In the former case the oxygen probably goes to produce physiological oxidation in the bacterial cell. Thus many aërobic organisms can grow in the absence of free oxygen, provided that nitrates are added to the medium, and these are thereby converted into nitrites (Pakes and Jollyman, Chem. Soc. Trans.

1901, 322; Ritter, Centr. Bakt. Par. ii. 1907–8, 20, 21).

The bacterial reduction of sulphates, thiosulphates, and sulphites to sulphuretted hydrogen is probably due to a similar action (Beyerinck, *ibid.* 1895, 1, 1).

The direct addition of hydrogen by bacteria to certain colouring matters is a well-recognised phenomenon. Thus many organisms readily reduce methylene blue to the leuco-compound, not only when grown in its presence, but also when the organisms are suspended in a solution of the colouring matter. The same effect is produced by dry sterile preparations obtained by treating the bacteria with acetone, and is ascribed to the action of a specific reducing enzyme or reducase, which becomes inactive at about 60° (Cathcart and Hahn, Arch. Hyg. 1902, 44, 295). The chemistry of the process has already been discussed under the heading of *Reducing enzymes.*

(*b*) **Denitrification.** One of the best-studied instances of deoxidation by bacteria is the process of denitrification, whereby nitrates are reduced to oxides of nitrogen, free nitrogen, and ammonia. The power possessed by many bacteria of reducing nitrates to nitrites was observed as early as 1875 (Meusel), and has been investigated by many authors since that date (Frankland, Chem. News, 1888, 57, 89; Warington, *ibid.* 1888, 57, 246; Maasen, Arbeit. K. Gesund-Amt. 1901, 18, 21; Grimbert, Ann. Inst. Pasteur, 1899, 13, 67; Franzen and Löhmann, Zeitsch. physiol. Chem. 1909, 63, 52). The reduction to nitrite occurs in nitrate broth, is accompanied by the evolution of carbon dioxide, and, as mentioned above, is probably due to direct deoxidation, as it is effected by many bacteria which do not produce free hydrogen. The production of ammonia from nitrates is also apparently a common property of bacteria, but the relations in this case have not been so clearly established as in that of nitrite. The evolution of oxides of nitrogen from a fermenting liquid was observed by Dubrunfaut (1868), in the case of fermenting molasses; but the production of the oxides was ascribed to purely chemical causes. Since that time, however, the production of nitrous and nitric oxides from nitrites by bacteria has been frequently observed in mixed fermentations. With pure cultures the phenomenon is much less common, but an organism known as *B. denitrificans* (Stutzer and Burri), which is however probably identical with *B. pyocyaneus* (Flügge), has been described, which ordinarily reduces nitrates to nitrogen, but in presence of asparagine produces nitric oxide (Gayon and Dupetit, Chem. Soc. Abstr. 1886, 823). Another organism, *B. nitroxus* (Bey. and Mink.), is chiefly responsible, according to Beyerinck and Minkmann (Centr. Bakt. Par. ii. 1909, 25; 30) for the almost universal occurrence of nitrous oxide in the gases produced when soil is added to nitrate broth. So vigorous is this process that a stream of gas may be obtained containing 80 p.c. of nitrous oxide, and capable of relighting a glowing splint. *B. pyocyaneus*, *B. Stutzeri* (L. and N.), and *M. denitrificans* (Bey. and Mink.), all produce nitrous oxide from nitrates. On the other hand, *B. Hartlebii*, under anaërobic conditions, produces from a nitrate and a tartrate or lactate such a considerable amount of nitric oxide that brown fumes are seen when air is led into the flask (Lebedev, A. J., Ber. deutsch. bot. Ges. 1911, 29, 327).

Finally, in many cases, the reducing action of bacteria on nitrates proceeds as far as the production of free nitrogen. This phenomenon, since it was first attributed to bacterial action by Gayon and Dupetit in 1882 (Compt. rend. 1882, 95, 664), has been the subject of numerous investigations, on account of its importance in agriculture, since it may occur both in soil and in manure. It has been conclusively established that, in presence of suitable carbonaceous nutriment, nitrates are readily decomposed in this way by many bacteria, especially in the absence or scarcity of oxygen. Jensen has shown (Centr. Bakt. Par. ii. 1897, 3, 622; 1898, 4, 401) that in these cases the oxygen of the nitrate is utilised for the oxidation of the organic matter, and that the presence of free oxygen greatly diminishes the extent of the denitrification. It seems probable that the 'nitrogen' estimated by the older observers was really a mixture of nitrogen and nitrous oxide.

The serious loss of nitrogen which occurs in manure heaps, and may amount to as much as 25 p.c. of the total nitrogen in three months, or 50 p.c. in nine months, has been investigated by many authors (*see* Russell and Richards, J. Agri. Sci. 1917, 8, 495, where the literature is quoted). The phenomenon depends on the alternation of aërobic and anaërobic conditions, and may possibly be due to bacterial oxidation of the nitrogenous matter to nitrate, followed by denitrification. It has not, however, been proved that this is the actual course of events, and Russell and Richards consider that the process may be explained by the supposition that under anaërobic conditions a change is effected by bacterial action which leaves some of the nitrogen compounds present in such a condition that subsequent oxidation decomposes them with evolution of nitrogen. A similar loss of nitrogen occurs in the filtration of sewage.

Putrefaction. Decomposition of amino-acids. The term 'putrefaction' is usually applied to the decomposition which is set up by bacteria in animal and vegetable remains at the ordinary temperature, and which is accompanied by the production of malodorous compounds and gases. The chief source of these is the protein matter of the organism, so that the characteristic feature of putrefaction is the bacterial decomposition of proteins. The process consists chemically in a hydrolysis of the proteins into simpler molecules, followed or accompanied by the decomposition of these, yielding, according to circumstances, highly oxidised substances or a series of reduction products. In the presence of an abundant supply of oxygen, the process continues until the final products are carbon dioxide, water, ammonia, and mineral salts, whereas in a limited supply or in absence of oxygen, a whole series of compounds is formed comprising bases, acids, volatile sulphur compounds, &c.; and this is the characteristic phenomenon known as putrefaction. Similar chemical changes are produced when proteins are fused with caustic alkalis at 250° (Gautier and Étard, Compt. rend. 1882, 94, 1357).

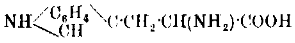
The immediate origin of the products of putrefaction is then to be sought in the various products of hydrolysis of the proteins. These consist, as is well known, chiefly of amino-acids, diamino-acids, such as arginine and lysine, and a number of other compounds. As of special importance may be mentioned histidine, or β-iminazole-α-aminopropionic acid (α-amino-β-glyoxaline-4 (or 5)-propionic acid), tryptophan or indole-α-aminopropionic acid, and cystine $(COOH·CH(NH_2)·CH_2·S)_2$.

The amino-acids undergo decomposition in at least two different ways. In the first place, the amino group may be removed by reduction (deaminisation), yielding the corresponding fatty acid (equation *a*), which then either undergoes oxidation (equation *b*), yielding a lower acid or simply loses carbon dioxide (equation *c*):

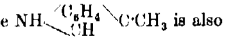
$$(a) R·CH(NH_2)·COOH+2H=R·CH_2·COOH+NH_3$$
$$(b) R·CH_2·COOH+3O=R·COOH+H_2O+CO_2$$
$$(c) R·CH_2·COOH=R·CH_3+CO_2$$

Thus leucine $(CH_3)_2CH·CH_2·CH(NH_2)·COOH$ yields valeric acid, and it is probable that formic, acetic, propionic, butyric, and caproic acids, which are all present in the products of putrefaction, are formed in a similar way.

Of special interest are the products obtained in this way from tryptophan, a substance which was discovered by Hopkins and Cole (J. Physiol. 1902, 27, 418), among the products of hydrolysis of proteins by trypsin, and which is the mother substance of the various indole derivatives to which the characteristic odour of fæces is largely due. Tryptophan has been found by Ellinger (Ber. 1907, 40, 3029) to be indole-*a*-aminopropionic acid, of the formula



$$NH\begin{matrix}\diagup C_6H_4 \diagdown \\ \diagdown CH \diagup\end{matrix}C·CH_2·CH(NH_2)·COOH$$

and is decomposed by putrefaction in the manner described above, yielding successively indolepropionic acid $C_8H_6N·CH_2·CH_2·COOH$, indoleacetic acid $C_8H_6N·CH_2·COOH$, and indole C_8H_7N. A certain amount of skatole or α-methylindole  $NH\begin{matrix}\diagup C_6H_4 \diagdown \\ \diagdown CH \diagup\end{matrix}C·CH_3$ is also formed, probably by a reaction of the type (c) given above. By similar reactions phenylalanine $C_6H_5·CH_2·CH(NH_2)·COOH$ yields successively phenylpropionic acid, phenylacetic acid, and benzoic acid, whilst tyrosine, or *p*-hydroxyphenylaminopropionic acid

$$OH·C_6H_4·CH_2·CH(NH_2)·COOH$$

is converted into *p*-hydroxyphenylpropionic acid (hydroparacumaric acid, Baumann, 1879), *p*-hydroxyphenylacetic acid (Salkowski, E. and H., Ber. 1879, 12, 648; 1880, 13, 189, 2217), *p*-cresol, *p*-hydroxybenzoic acid, and phenol. In an abundant supply of oxygen even these simple aromatic compounds are completely oxidised; thus a bacillus has been isolated which in pure culture readily oxidises dilute solutions of phenol (Fowler, Ardern, and Lockett, Proc. Roy. Soc. B, 1910, 83, 149).

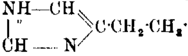
Succinic acid, which is always formed in putrefaction, is probably derived from aspartic acid $COOH·CH_2·CH(NH_2)·COOH$ by reduction (Salkowski).

It is not improbable that this type of decomposition of the amino-acids may be accompanied by the type of decomposition which is brought about by yeast in presence of sugar and has already been discussed the characteristic feature of which is that the amino group is removed with formation of a keto acid, which then undergoes further decomposition.

A second extremely important mode of decomposition of the amino-acids, diamino-acids, &c., during putrefaction, is the simple elimination of carbon dioxide, leading to the formation of bases (decarboxylation):

$$(d) R·CH(NH_2)·COOH=R·CH_2·NH_2+CO_2$$
$$(e) \underset{\text{Lysine.}}{NH_2·CH_2·CH_2·CH_2·CH(NH_2)·COOH} = \underset{\text{Cadaverine.}}{NH_2[CH_2]_3·CH_2·NH_2}+CO_2$$

Many bases have been isolated from putrefying mixtures, and great importance is to be attached to their formation, inasmuch as several of them have a very marked physiological action. The observation that putrefying flesh may contain poisonous basic substances, liable to be confused with the vegetable alkaloids, was made by Selmi (1872), who gave to these bases of animal origin the name ptomaines (πτῶμα, a corpse), and they were then more thoroughly investigated by Brieger. It was at first thought that the poisonous products which result from the action of bacteria on various culture media and on meat, fish, &c., were also members of this class, and the effect of pathogenic bacteria on the living organism was ascribed to the production of these same substances in the system, a view to which the term 'ptomaine-poisoning,' still erroneously applied to case of meat-poisoning, &c., gives expression. It has now however, been found that the characteristic and specific poisons produced by bacteria are probably much more complex in their structure, and belong more probably to the class of proteins than to that of the ptomaines. They are termed toxins or bacterial toxins, and are distinguished as ectotoxins, which pass out of the bacterial cell into the surrounding medium (as do diphtheria toxin and tetanus toxin), and endotoxins, which are retained within the cell, but appear to pass out of it after death (typhoid toxin, &c.).

The origin of many of the simple mono- and di-acid bases which occur in putrefaction can be traced to the corresponding amino acids, among these being *iso*amylamine derived from leucine, phenylethylamine derived from phenylalanine, *p*-hydroxyphenylethylamine derived from tyrosine, and β-iminazolylethylamine (histamine)  $\begin{matrix}NH—CH \\ | \quad\quad \\ CH — N\end{matrix}\!\!\!>C·CH_2·CH_2·NH_2$ derived from histidine, all of which have a very marked effect in raising the blood pressure, or in other ways, and are of physiological importance because they are in all probability formed in the intestine and absorbed (Barger and Walpole, J. physiol. 1909, 38, 343; Barger and Dale, *ibid.* 1910, 41, 19, 499). Bacteria capable of decomposing histidine in this way have actually been isolated from the intestine (Mellanby and Twort, J. Physiol. 1912, 45, 53; Berthelot and Bertrand, Compt. rend. 1912, 154, 1643, 1826). Of the diamino-bases isolated by Brieger may be mentioned ethylenediamine $NH_2·CH_2·CH_2·NH_2$, putrescine or tetramethylenediamine

$$NH_2·[CH_2]_4·NH_2$$

derived from arginine, cadaverine or pentamethylenediamine derived from lysine (equation *e*).

In addition to these, trimethylamine, choline $CH_2(OH)\cdot CH_2\cdot N(CH_3)_3OH$, muscarine

$$CH(OH)_2CH_2\cdot N(CH_3)_3OH$$

and neurine $CH_2:CH\cdot N(CH_3)_3OH$, of which the last two are highly poisonous, all occur, probably derived not from proteins, but from lecithin and its allies, which yield, on hydrolysis, glycerol-phosphoric acid, fatty acids, amino-ethyl alcohol, and choline.

Finally, an invariable product of the action of bacteria on proteins is ammonia, formed either by reduction of amino-acids as explained above, or by their oxidation. This bacterial production of ammonia (ammonification) is a process of fundamental importance in the soil, since, as already described, ammonia serves as the raw material for the production of nitrate. According to Marchal (Chem. Soc. Abstr. 1894, ii. 248), a large number of bacteria are concerned in the process, the most active among them being *B. mycoides*.

In the decomposition of histidine, which contains nitrogen both in the iminazole nucleus and in the side chain, ammonia is produced from both sources by the aerobic action of many bacteria (*B. paratyphosus*, A and *B*, *B. fæcalis alcaligenes*, *B. pyocyaneus*), whereas *B. vulgaris* (*proteus*) only attacks the side chain (Raistrick, Biochem. J. 1919, 4, 446). Many bacteria of the coli-typhosus group yield with histidine $C_3H_3N_2\cdot CH_2\cdot CH(NH_2)\cdot COOH$, the unsaturated urocanic acid

$$C_3H_3N_2\cdot CH:CH\cdot COOH$$

formed possibly by direct elimination of NH_2 and H from the side chain (Raistrick, Biochem. J. 1917, 11, 71).

The gases evolved consist of carbon dioxide, hydrogen, and sometimes methane, nitrogen, and sulphuretted hydrogen. Some of the sulphur of the proteins is converted into methylmercaptan (Nencki), and traces of many other sulphur compounds are formed, these being the main cause of the characteristic smell. The phosphorus is chiefly converted into phosphate, the evolution of phosphine alleged by some observers being doubtful.

The organisms which bring about these characteristic changes are very numerous. Usually many different organisms are present, and there seems little doubt that in some cases the various stages of decomposition are effected by different species of bacteria. Reference has already been made to the effect of the presence or absence of air, but this affects not only the chemical changes produced, but also the nature of the bacterial flora. In a free supply of air the organisms are mainly aërobic, whereas in a limited supply anaërobic organisms are chiefly present. Frequently the surface of the putrefying mass is occupied by aërobic organisms, and these use up the oxygen, and provide suitable conditions for the development of anaërobes at a lower stratum. It appears also that the primary proteins are directly attacked and digested by one group of organisms, those which produce an ecto-proteoclastic enzyme, whilst a second group possessing insoluble endo-proteoclastic enzymes, is only able to decompose the simpler products formed by this hydrolysis.

Of the actual organisms which are usually present there may be mentioned *B. vulgaris* (L. and N.) (formerly known as *proteus*), *B. fluorescens liquefaciens*, *B. mesentericus* (L. and N.), all of which attack and digest albumins. *B. sporogenes* (Metchnikoff) and *B. histolyticus* (Weinberg and Séguin), which have been found in infected wounds, both attack proteins with the production of large amounts of amino-acids, whilst the latter forms both gas and volatile acids from meat (Wolf and Harris, J. Path. Bact. 1907, 21, 386; 1918, 22, 1). The organism formerly known as *B. putrificus* (Bienstock) and regarded as one of the most characteristic putrefactive organisms is probably a mixture of the two sporing anerobes, *B. sporogenes* (Metch.) and *B. cochlearius* (Douglas, Fleming and Colebook). Belonging to the second group, which only decompose simpler proteins, are *B. coli communis* and its allies, the characteristic bacilli of the large intestine, many of which produce indole and indole-acetic acid, *B. prodigiosus* (Flügge), *Streptococcus pyogenes* (Rosenbach), &c. In any particular case the flora is largely conditioned by the exact nature of the putrefying material, so that meat, fish, milk, eggs, &c., all have their characteristic organisms and modes of decomposition.

FERMENTATIONS PRODUCED BY MOULDS.

A number of moulds, especially belonging to the families *Aspergillaceæ* and *Mucoraceæ*, are distinguished by producing definite chemical changes of a fermentative character, some of them by the secretion of soluble enzymes, and others by means of endoenzymes.

Alcoholic fermentation. The power of producing alcoholic fermentation is common to a large number of the *Mucoraceæ*, but is only possessed to any considerable extent by a single species of the *Aspergillaceæ*. *Allescheria Gayoni* (Saccardo and Sydow = *Eurotiopsis Gayoni*, Cost.) appears to be capable of producing a typical alcoholic fermentation of glucose, lævulose, maltose, and lactose, producing as much as 8 p.c. of alcohol in the medium, and forming glycerol and succinic acid in a similar manner to yeast.

The alcoholic fermentation produced by many species of *Mucor* has long been a subject of interest. When the mycelium of *M. racemosus* (Fres.), for example, is submerged in a nutrient medium containing sugar, alcoholic fermentation occurs, and at the same time the mycelium breaks up into spherical cells, which continue to grow by budding, and have hence been termed spherical yeast. The opinion has been held at various times that these cells were true yeasts, and moreover that all yeast had a similar origin. The first statement has now been definitely disproved, and no satisfactory evidence exists in favour of the second. It was further thought that when growing in the normal manner on the surface of the liquid, the mucor had only the power of oxidising the glucose, but that when submerged and thus deprived of a free supply of air, it became able to ferment it (Pasteur). It has, however, been established by the work of Wehmer (Centr. Bakt. Par. ii. 1905, 14, 556; 15, 8) and Kostytschev (*ibid.* 1904, 13, 490) that the mould produces just as much alcohol in presence of a free supply of air as when submerged, and that the commencement of alcoholic fermentation and the production of spherical yeast cells are not causally connected. A very large number of species of *Mucor* and *Rhizopus* have been carefully examined as to their power of producing alcohol and fermenting the polysaccharides (*see* Wehmer, article in Lafar, Technische Mykologie, iv. 517).

Production of diastase. Some species of these two families produce such large amounts of diastatic enzyme that they have been employed both industrially and domestically for the saccharification of starch, and a considerable number, if not all of them, produce a certain amount of this enzyme.

Mucor rouxii (Calm.), Wehmer (*Amylomyces rouxii*), was isolated by Calmette from Chinese yeast, and is employed in pure culture for converting the starch in a sterilised distillery wash into sugar, which is then fermented by a pure culture of yeast and distilled. (*See* Chapman, Cantor Lectures, 1921.)

Aspergillus oryzæ (Ahlburg), Cohn, has long been employed in Japan for the preparation of saké from rice, and of the soya sauce from the soya bean. The diastase of this organism, known as takadiastase, acts on starch much more energetically than malt diastase.

The oxalic acid fermentation. A very remarkable instance of oxidative fermentation is afforded by *Aspergillus niger* (van Tieghem) (*Sterigmatocystis nigra*), which converts glucose into oxalic acid. When this mould is grown on a nutrient solution containing glucose at 15°–20°, free oxalic acid is produced, the acidity increases up to a maximum, and then gradually diminishes and finally disappears. If, however, calcium carbonate or an alkaline phosphate be added, the oxalic acid accumulates, either as insoluble calcium oxalate or as an acid oxalate. In this way, for example, 1·5 grams glucose yielded 1·05 grams of oxalic acid in the form of calcium oxalate, whereas in the absence of chalk the maximum amount was 0·298 gram. The complete conversion of all the carbon of the glucose into oxalic acid would yield about 2·25 grams, so that the yield is approximately 50 p.c., the remainder of the glucose being presumably used for the needs of the organism (Wehmer, Ber. Bot. 1891, 9, 223, 163; Bot. Zeit. 1891, 49, 233; Annalen, 1892, 269, 383). As regards the mechanism of this action, Raistrick and Clark (Biochem. J. 1919, 14, 329) have found that oxalic acid is freely produced by this organism from succinic, fumaric, malic, and tartaric acids, and from acetic acid, but not from monobasic acids containing four atoms of carbon, from three-carbon acids or from glycollic, glyoxylic, or formic acids. They conclude that the oxalic acid is in part produced by oxidation of acetic acid formed from the sugar with intermediate production first of β.δ-diketoadipic acid

$$COOH{\cdot}C(OH):CH{\cdot}C(OH):CH{\cdot}COOH$$

which then yields acetic acid and oxalacetic acids $COOH{\cdot}CH:C(OH){\cdot}COOH$, the latter of which undergoes hydrolysis to oxalic and acetic acids. Many species of *Penicillium* produce small amounts of oxalic acid, and one of them, *P. oxalicum* (Thom), which occurs on mouldy corn, gives yields almost equal to these obtained from *A. niger*, producing the acid readily from both glucose and starch (Currie and Thom, J. Biol. Chem. 1915, 22, 287).

The citric acid fermentation. Whereas *Aspergillus niger* produces oxalic acid from glucose, other members of the *Aspergillaceæ*, *Citromyces Pfefferianus* and *C. Glaber*, described by Wehmer; and *C. citricus*, *C. tartaricus*, and *C. oxalicus*, described by Mazé and Perrier (Compt. rend. 1904, 139, 311; Ann. Inst. Pasteur, 1904, 18, 553), convert this sugar into citric acid. According to Currie, however (J. Biol. Chem. 1917, 31, 15), citric acid is also formed by *A. niger*, and is in this case to be regarded as an intermediate stage in the formation of oxalic acid, which is readily produced by this organism from citric acid. Wehmer states that as in the case of oxalic acid, the citric acid is further oxidised if it be allowed to remain in the free state in the presence of the organisms, but accumulates when it is converted into a salt by the addition of calcium carbonate. Currie, however, using *A. niger*, has found that the best yield of citric acid is obtained by growing the mould in an acid solution (P_H = 3·4–3·5) containing ammonium nitrate as the source of nitrogen. Under these circumstances the production of citric acid may amount to 66 p.c. of the saccharose employed, the acidity of the solution increasing until a P_H of 1·46 is reached. In presence of calcium carbonate about half the sugar can be converted into citric acid; thus, Buchner and Wustenfeld (Biochem. Zeitsch. 1909, 17, 395), working with *C. citricus*, found that the maximum amount of citric acid produced amounted to 56 p.c. of the sugar. A large amount of carbon dioxide was simultaneously evolved, corresponding in various experiments to the oxidation of 48–77 p.c. of the sugar, the citric acid in the same experiments amounting to 33–38 p.c. of the sugar, and the new growth of mould to 5–31 p.c. of the sugar. The characteristic formation of citric acid could not be obtained with press juice nor with acetone preparations of the mycelium. Citric acid is also formed from glycerol and from alcohol, as well as in small quantities *in vacuó* from the mycelium of the mould alone (Mazé and Perrier).

Mazé and Perrier regard the citric acid as a product of catabolism of the cell substance, induced by lack of nitrogen, and not as a true product of the oxidation of sugar; whereas Buchner and Wüstenfeld ascribe its formation to a process analogous to the production of parasaccharic acid

$$CH_2(OH){\cdot}CH(OH){\cdot}C(OH)(COOH){\cdot}CH_2{\cdot}CH_2(OH)$$

from lactose by milk of lime (Kiliani).

In their action on sugar and allied compounds the moulds differ very decidedly from the bacteria. The production of lactic, acetic, butyric, and formic acids, and the evolution of hydrogen and carbon dioxide, which are characteristic of so many bacterial actions, are not observed among the moulds. On the other hand, the latter are often capable of producing alcoholic fermentation, are richly endowed with the various hydrolytic enzymes, and, in some cases, produce compounds, which, like malic, oxalic, and citric acids, are characteristic of the higher plants.

Many other interesting chemical changes brought about by moulds have been observed, among which may be mentioned the production of fumaric acid from glucose and fructose by

Rhizopus nigricans (Ehrlich, Ber. 1911, 44, 3737), and the conversion of cinnamic acid into styrene by *A. niger* (Herzog and Ripke, Zeitsch. physiol. Chem. 1908, 57, 43).

Decomposition of amino-acids. The amino-acids are very readily oxidised by many moulds, both by living cultures and by the killed cells after treatment with acetone. In some cases the action is selective, only the naturally-occurring modification being attacked (Herzog and Meier, Zeitsch. physiol. Chem. 1908, 57, 35; Pringsheim, *ibid.* 1910, 65, 96).

Ehrlich has, however, observed (Ber. 1911, 44, 888) that in presence of sugar many fungi convert the amino-acids into the corresponding hydroxy-acids $R{\cdot}CH(NH_2){\cdot}COOH \rightarrow R{\cdot}CH(OH){\cdot}COOH$ and many amines into the corresponding alcohols (Ehrlich and Pistschimuka, Ber. 1912, 45, 1006). He has in this way, by the use of *Oidium lactis* (which can readily be isolated from sour milk or cheese), been able to prepare the optically active hydroxy-acids corresponding with tyrosine, phenylalanine, and tryptophan, which had not previously been obtained. Some fungi (*e.g. Monilia candida*) not only form the hydroxy-acid, but also act in a similar manner to yeast and convert a portion of the amino-acid into an alcohol by elimination of ammonia and carbon dioxide.

Urea, uric acid, and hippuric acid are hydrolysed by many moulds, the active agent being an enzyme present in the filtrates from cultures of the organisms (Kossowicz, Zeitsch. Garungsphysiol. 1912, 1, 60, 121, 137; 2, 51).

Authorities.—A very copious literature now exists on the subjects of fermentation, enzyme action, and chemical action of bacteria. The chief works consulted in the preparation of the foregoing article, in addition to the original papers, are:

Lafar, Technische Mykologie (Gustav Fischer, Jena), 4 vols., vol. v. in progress.

Oppenheimer. Die Fermente und Ihre Wirkungen, 3 vols. (Leipzig, F. C. W. Vogel, 1909–10).

Oppenheimer, Handbuch der Biochemie des Menschen und der Tiere (Jena, Gustav Fischer).

Buchner, H. and E., and Hahn. Die Zymasegärung (Oldenbourg, Berlin, 1903).

(Monographs on Biochemistry, Longmans, Green, & Co., London.)

Armstrong, The Simple Carbohydrates and Glucosides.

Barger, The Simpler Natural Bases.

Bayliss, The Nature of Enzyme Action.

Harden, Alcoholic Fermentation.

Russell, Soil Conditions and Plant Growth.

A. H.

FERNANDINITE. A hydrous calcium vanadyl vanadate $CaO{\cdot}V_2O_4{\cdot}5V_2O_5,14H_2O$, forming compact masses of a dull-green colour or minutely crystallised in rectangular plates. It dissolves readily in acids to a green solution, and sufficiently in cold water to give a yellow solution. It occurs as an alteration product of patronite at Minasragra in Peru. L. J. S.

FERONIA GUM *v.* GUMS.

FERONUCLIN. Trade name for dry yeast extract.

FERRATES *v.* IRON.

FERRATOGEN or **FERRINOL.** Syn. for iron nucleinate.

FERRIC ACETATE *v.* ACETIC ACID.

FERRIC SALTS *v.* IRON.

FERRICHTHOL. Trade name for an ichthyol preparation of iron.

FERRITE. This term has unfortunately several different meanings. To the chemist it implies a salt in which ferric oxide plays the part of an acid, for example, barium ferrite $BaFe_2O_4$. In a mineralogical sense it was first applied by H. Vogelsang, in 1872, to an amorphous iron hydroxide, of unknown composition, which, as red and yellow particles, is present in many partially decomposed igneous rocks. In this sense the term is much used by certain petrologists for the patches of indefinite ferruginous alteration products seen under the microscope in thin sections of rocks. The same name has also been applied to ferruginous pseudomorphs after olivine occurring in the doleritic rocks of the neighbourhood of Glasgow (M. F. Heddle, Min. Mag. 1882, 1887). It has also been much used by metallographers, following H. M. Howe (The Metallurgy of Steel, 1890), for pure metallic iron, which, together with iron carbide, &c., forms one of the microscopic constituents of iron and steel. Later, the same name was applied by V. I. Vernadsky, in his Russian Treatise on Mineralogy (Petrograd, 1908), to native iron, for example, the terrestrial iron from Uifak on Disco Island, Greenland. L. J. S.

FERRITE (*v. supra*) the name given to the carbon-free constituent of steels. Usually it is nearly pure iron, but in special steels it may be an alloy of iron with silicon, chromium, tungsten, &c. Ferrite exists in three forms: α-iron, stable up to 760°; β-iron, stable between 760° and 900°; and γ-iron, stable above 900°. Of these, γ-iron is the hardest (Howe, Metallographist, 1898, i. 259). The freezing-point of ferrite is 1505° (Carpenter, J. Iron and Steel Institute, 1908, iii. 290; Saklatwalla, *ibid.* ii. 92).

Under the microscope ferrite is characterised by its softness, and the cubic structure revealed by deep etching with acids or cupric ammonium chloride (Andrews, Engineering, 1895, 88; Stead, J. Iron and Steel Institute, 1898, i. 145).

FERRITUNGSTITE *v.* TUNGSTITE.

FERROCHROME, FERROMANGANESE, FERROSILICON, FERROTITANIUM, FERROTUNGSTEN, FERROVANADIUM *v.* IRON.

FERROCYANIDES *v.* CYANIDES.

FERROPYRINE (*Ferripyrine*). Trade name for antipyrine ferric chloride. Obtained by the interaction of antipyrine and ferric chloride in aqueous solution. Used as an hæmostatic and astringent.

FERROTYPE *v.* PHOTOGRAPHY.

FERROUS ACETATE *v.* ACETIC ACID.

FERTILISERS or MANURES. Either of these terms might properly be applied to any material added to the soil for the purpose of increasing its fertility, and, in this sense, would be extended to include lime, chalk, marl, and even clay and sand. In common practice, however, the term 'manure' or 'fertiliser' is restricted to materials the main function of which is to convey directly to the soil some constituent or constituents of plant food, to the exclusion of those of which the fertilising action is mainly indirect, consisting in the improvement of the physical condition of the soil or the development of its inherent or natural chemical resources. The chief constituents of plant food which are naturally taken up from the soil are nitrogen, phosphorus, sulphur, potassium, calcium, magnesium, and iron, together with the less important constituents silicon, chlorine, and sodium. A manure or fertiliser, in the sense in which the term is ordinarily used, will always contain one or more of these substances.

Apart from calcium—the supply of which is necessary in special cases only—nitrogen, phosphorus, and potassium are by far the most important constituents to be applied as manure, as they are those in which the soil is most generally deficient.

In an efficient fertiliser the constituents must be in a condition suitable for immediate assimilation by the plant, or must be capable of speedily acquiring this condition after mixing with the soil. Manures or fertilisers are sometimes classified as 'natural' and 'artificial,' but the dividing line is not always easily drawn. In the present article we shall briefly consider the principal substances employed as manures or fertilisers, passing on to some observations as to the general relative utility of some of them, and shall then refer to the special methods employed for their analysis.

Farmyard manure. Farmyard manure and stable manure are composed of litter mixed with the excreta of animals. The litter in farmyards is usually straw, but this has been to a large and increasing extent superseded in stables by dried and shredded peat moss. In some parts of the country bracken is used for litter, and in hop districts hop-bine is thus worked up into manure. The composition of the manure depends initially to some extent on the nature of the litter, but to a greater extent on the length of time the litter has been in use, the number and kind of animals littered on it, and the quantity and quality of the food consumed by them. Its final value—that is to say, its value at the time of its application to the land—is also largely governed by the mode of 'making,' and the mode and duration of storage. Its valuable effect on the soil may be said to be twofold. In virtue of the large quantity of bulky organic or carbonaceous matter that it contains, it improves the physical condition of the soil, making 'heavy' soils more 'open,' and 'light' soils more retentive. At the same time, it returns to the land the mineral matter and much of the nitrogen previously removed from it in the form of straw, as well as much of the nitrogen and most of the phosphoric acid and potash derived from home-grown fodder consumed during its production, reinforced by similar matter derived from the simultaneous consumption of additional purchased food.

The proportion of the nitrogen and manurially available 'mineral' matters absorbed and retained by animals from their food depends upon their age, condition, and other circumstances. Thus, a young growing steer, or a cow in milk, will assimilate more nitrogen and phosphates, and consequently void less in the form of fæces and urine, than will a fattening ox, which has already built up its frame and principal nitrogenous tissues, and is increasing its weight mainly by the production of fat. Thus the quantity of nitrogen voided in fæces and urine might vary from more than 95 p.c. of the nitrogen consumed in the food to as little as 75 p.c. The proportion of phosphoric acid and potash voided will be greater. Obviously, in the case of horses, which only spend a portion of their time in the stable, only a fraction of the excreta will be mingled with the litter; and so also in the case of cattle which are turned out for a part of their time. It is manifestly only the stall-fed or yard-fed animal which contributes the whole of the nitrogen, phosphates, and potash which it voids to the actual manure heap.

Unfortunately for the farmer, the fertilising matter thus initially contributed to the manure is by no means all ultimately available for utilisation. Continual losses occur. These are at their highest in an open farmyard exposed to the weather, where more or less loss of the valuable soluble constituents of the manure is always going on by mere drainage, and where there is the greatest facility for the evaporation of ammonia. They are at their lowest where the animals are fed in close boxes, in which the litter is trodden down compactly in watertight pits; but even here there is constant loss by reason of fermentative action, not only through evaporation of ammonia, but also by the reduction of ammonia and other easily decomposable nitrogenous compounds into free nitrogen. The losses that thus occur have been studied by numerous investigators, including Lawes and Gilbert, A. Voelcker, J. A. Voelcker, Hall, Maercker, and Schneidewind, Holdefleiss, Müntz and Girard, Wood, Russell, and numerous others. The general result has been to show that, even under the best conditions of ordinary production, the loss of nitrogen may be expected to amount to about 15 p.c. by the time the manure is taken out of the boxes, while in shallow stalls or yards it may amount to 30 or 40 p.c. Further loss of nitrogen takes place after the manure is heaped or stacked for 'ripening,' or for preservation until it is convenient to transfer it to the land. It is probable that, even with fairly good management, the ultimate loss of nitrogen may amount on the average to 50 p.c. of the initial quantity. Under bad management, especially with open yards and free drainage, it is probably often much greater.

Various plans have been adopted or suggested for checking the loss, such as the use of gypsum or superphosphate sprinkled in the manure during its accumulation, to absorb ammonia; or of kainit, which checks fermentation. In any case the manure should be heaped as compactly as possible, with layers of earth in it, and the heap should be covered with earth. It has been demonstrated that the greatest percentage loss of nitrogen unfortunately occurs in the manure that is initially richest, namely, that produced by animals liberally fed on highly nitrogenous food.

It is obviously difficult to give an average composition for so variable a substance as farmyard manure, but broadly it may be said to consist of:

Water	**about 75 p.c.**
Organic and volatile matter	**„ 22 „**
Mineral matter (exclusive of earth)	**„ 2½–3 „**

But, as the water may vary from perhaps as little as 65 p.c. to over 80 p.c., the quantity of organic matter is liable to considerable inverse variation. The proportion of nitrogen is usually from about 0·45 to 0·65 p.c., that of potash from about 0·4 to 0·8 p.c., and that of phosphoric acid from about 0·2 to about 0·4 p.c.

Hall gives the following tables illustrating the general composition of farmyard manure, and also showing the influence of feeding on the nitrogen contents of the manure :—

COMPOSITION OF FARMYARD MANURE FROM VARIOUS SOURCES (HALL).

—	Water	Nitrogen	Phosphoric acid	Potash
	p.c.	p.c	p.c	p.c.
1. Fresh long straw manure	66·17	0·544	0·318	0·673
2. No. 1 after rotting .	75·4	0·597	0·454	0·491
3. Very old and short, from a mushroom bed .	53·14	0·80	0·63	0·67
4. Fresh } French data .	75·0	0·39	0·18	0·45
5. Rotten } French data .	75·0	0·50	0·26	0·53
6. Very old } French data .	79·0	0·58	0·30	0·50
7. Rothamsted average .	76·0	0·64	0·23	0·32
8. Fresh liquid manure .	98·02	0·044	0·051	0·355
9. Old ditto . . .	99·13	0·026	0·014	0·22

PERCENTAGE COMPOSITION OF FARMYARD MANURE (HALL).

Diet	Year	Dry matter	Total nitrogen	Nitrogen as ammonia	Nitrogen as amides	Insoluble nitrogen	
Roots and hay only	1904	23·6	0·577	0·046	0·067	0·464	Made into mixen & stored
Cake-fed	1904	24·03	0·716	0·079	0·096	0·541	
Roots and hay only	1905	29·5	0·462	0·040	0·047	0·375	Do.
Cake-fed	1905	31·3	0·698	0·182	0·055	0·461	
Roots and hay only	1906	22·0	0·466	0·220	0·033	0·411	Do.
Cake-fed	1906	24·3	0·690	0·097	0·049	0·544	
Roots and hay only	1907	25·3	0·589	0·125	0·053	0·411	Not stored
Cake-fed	1907	25·5	0·815	0·377	0·033	0·405	

Straw manure will contain more potash than peat moss manure, but the latter contains more nitrogen. Stable manure is 'hotter'—that is to say, ferments more rapidly—than farmyard manure proper. Very large quantities are purchased from town stables by market gardeners and other farmers within easy carriage of cities. This largely consists of litter that a farmer would regard as only half used, owing to the necessity for the prompt clearing of town stables; and it is necessarily poor in soluble nitrogen compared with farmyard manure. Analyses by Dyer (tabulated by Hall) (see next column) illustrate the composition of specimens of such manure, made both with straw and with peat moss, fresh and after some months' storage in heap on the farm of the purchaser.

In addition to its 'mineral' constituents (phosphates, potash salts, &c.), well-made farmyard manure contains enough available nitrogen in the form of ammonia compounds and easily nitrifiable organic matters to enable it to begin to act as plant food immediately; while it has at the same time a reserve of insoluble matter, partially decomposed organic matter which yields up nitrogen more slowly and gradually, the effect of much of which is realised only in subsequent seasons.

COMPOSITION OF LONDON STABLE MANURE (DYER—TABULATED BY HALL).

—	From peat moss	From straw	From mixed peat moss and straw				
			Fresh		After storage		
			1	2	1	2	3
Water .	77·80	70·0	76·1	62·0	58·8	61·0	52·9
Organic matter	18·00	24·3	19·3	26·4	17·5	22·0	23·0
Nitrogen, sol.	0·51	0·52	0·08	0·08	0·06	0·08	0·10
,, insol.	0·37	0·10	0·46	0·62	0·58	0·68	0·79
Phosphoric acid	0·37	0·48	0·33	0·45	0·49	0·56	0·60
Potash .	1·02	0·59	0·45	0·58	0·58	0·65	0·80

The duration of the action of farmyard manure largely depends upon the nature of the soil. In some 'open,' 'hot,' gravelly soils, farmyard manure is used up with remarkable rapidity. On other soils, its action may be spread over a considerable number of years; but in such cases its fertilising effect, especially on arable land, diminishes to an increasing extent each year, until, under the circumstances of ordinary farming, it becomes imperceptible. There are, however, experimental plots at Rothamsted, where, under circumstances peculiarly favourable to its operation, the effects of early dressings of farmyard manure are still evident after the lapse of 40 or 50 years.

The valuation of the unexhausted effect of farmyard manure in relation to the feeding stuffs consumed in producing it, is an important matter in the application of the Agricultural Holdings Act. This subject is fully discussed by Hall and Voelcker in a paper 'On the Valuation of the Unexhausted Manure obtained by the Consumption of Foods by Stock,' in the Journal of the Royal Agricultural Society of England, 1913, vol. 74 (also republished as a separate pamphlet by John Murray, of Albemarle Street, London, W.). In this paper the original valuation tables of Lawes and Gilbert were revised in the light of later investigation, and, with occasional revision to fit market prices, have been adopted by the Central Association of Tenant Right Valuers.

The general chemistry of farmyard manure has been well treated by Hall in his work on Fertilisers and Manures (Murray), and more fully recently by Russell and Richards (Journal Agric. Science, vol. viii. p. 495, 1917).

Peruvian guano. Guano was originally introduced into England from Peru in 1839, and for many years it occupied the first place among concentrated fertilisers. The original rich deposits have been for a long time exhausted, but considerable importations of Peruvian guano are still made, chiefly from recent deposits. Guano is formed from the excrement and carcases of sea-fowl. The fresh excrements are highly nitrogenous, and consist chiefly of uric acid and calcium phosphate. If the climate is hot and dry, the excrements are quickly desiccated and the nitrogenous matter protected. These conditions exist on the rainless coast of

Peru. In a moist climate the nitrogenous matter is quickly converted into ammonia and dissipated by evaporation or drainage, a phosphatic guano practically destitute of nitrogen remaining. The main supply of Peruvian guano for 30 years was from the Chincha Islands, which yielded, in all, from what we may call the original deposits, about 10,000,000 tons. This guano was a dry, excellent fertiliser, containing from 13 to 14 p.c. of nitrogen, and from 13 to 14 p.c. of phosphoric acid. On its exhaustion, about the year 1868, guano was shipped from the Guanape and Macabi Islands. This was a damp guano containing from 9 to 11 p.c. of nitrogen, and about 12–14 p.c. of phosphoric acid. This was succeeded by importations, still from old deposits, from the Ballestas Islands and the islands of Lobos de Afuera, and deposits on the mainland at Pabellon de Pica, Punta de Lobos, and Huanillos. Many of these deposits were of low nitrogenous content, but very rich in phosphates, while some possessed very much the character of the original Chincha guano. In more recent years shipments have been coming in from new deposits formed on the original islands, which have again become 'guaniferous,' the birds being now specially preserved with a view to the constant renewal of the deposits and the consequent maintenance of the output. These deposits of fresh guano are highly nitrogenous, and would be much richer in percentage composition but for the fact that a good deal of sand is sometimes unavoidably mixed with them.

The nitrogen in Peruvian guano is partly in the form of ammonia salts and partly in organic combination; and in some cases small quantities of nitrate are also present. The main part of the phosphoric acid is in the form of finely divided calcium phosphate, some of the phosphoric acid also being in combination with ammonium, sodium, or potassium. Some of the phosphoric acid, therefore, is immediately soluble in water, while even that which is insoluble is readily attacked by weak acids and rapidly available as plant food. There is also present an appreciable quantity of potash salts. Guano is, therefore, an extremely valuable manure, and has always commanded relatively higher prices than most other concentrated fertilisers. Having regard to the great variation in the composition of different cargoes, it has been for many years the practice of the chief importers to prepare a mixed or 'equalised' Peruvian guano, containing a fixed percentage of nitrogen, for the sake of those users who wish for guano of constant composition; but the guano is also on sale in its unmixed or natural condition, at prices varying *pro rata* with its composition. It may be added that dissolved Peruvian guano, which was introduced by Messrs. Ohlendorff in 1864, and is still manufactured by their successors, the Anglo-Continental Guano Works, is Peruvian guano treated with sulphuric acid to fix the ammonia and render the phosphate nearly all soluble in water. It is a large article of manufacture, and is sold containing definite percentages of nitrogen and soluble phosphate.

Examples of analyses of Peruvian guano of different grades from several of the islands given below, are historically interesting.

	Ballestas	Lobos d'Afuera	Cantores	Lobos de Tierra	South Guanape	North Guanape	Lobos d'Afuera		
Moisture	18·06	18·30	28·74	24·44	25·72	16·60	15·20	15·58	10·44
Organic matter and ammonium salts	40·36	36·32	35·66	32·16	29·91	29·50	26·55	19·57	11·96
*Phosphoric acid	9·74	10·62	13·25	11·84	14·79	16·35	15·07	17·21	19·13
Lime	9·21	10·53	11·45	10·75	12·25	13·08	12·46	14·17	14·50
†Magnesia, alkalis, &c.	7·93	9·61	9·10	8·64	9·84	11·92	10·65	11·27	12·32
Silicious matter	14·70	14·62	1·80	12·17	7·49	12·55	20·07	22·20	31·65
	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00
Total nitrogen	11·43	9·97	9·44	8·32	7·19	7·07	6·80	4·58	2·58
Equal to ammonia	13·88	12·11	11·46	10·10	8·73	8·58	8·26	5·56	3·13
*Equal to tricalcium phosphate	21·28	23·20	28·95	25·87	32·32	35·72	32·93	37·60	41·80
†Including potash	2·68	2·39	2·76	2·50	2·87	3·09	2·33	2·15	1·86

Besides Peruvian guano, the only other nitrogenous bird guanos of commercial importance have been obtained from Patagonia and from the Ichaboe Islands off the coast of Africa. Ichaboe guano, being from fresh deposits, is rich in nitrogen, of which it contains from 9 to 14 p.c. Its general composition is similar to that of Peruvian guano of similar grade. An appreciable proportion of the nitrogen, however, is in the form of feathers.

Seaweed. This is largely used in some localities near the sea. When quite fresh, seaweed contains about 80 p.c. of water. Its composition varies a good deal. The nitrogen may be 1–3 p.c. of the dry matter. The average percentage of potash in 20 analyses of *Fucus* and *Laminaria* was 3 p.c., and of phosphoric acid 0·5 p.c. of the dry matter. The proportion of nitrogen and potash in fresh seaweed is thus very similar to that in farmyard manure, while the phosphoric acid is deficient.

Fish manure or fish guano. Whole fish are employed as manure in places near the sea. Way found in fresh sprats 63·7 p.c. water, 1·94 p.c. nitrogen, and 2·1 p.c. ash, including 0·43 potash and 0·90 phosphoric acid.

Fish manure, or 'fish guano,' as it is called, is made on a considerable scale from various kinds of fish refuse. The Norwegian fish guano is prepared from cod. Herrings, sprats, menhadden, and other oily fish are boiled and pressed for the sake of their oil, and the residue is dried, powdered, and sold as fish guano. This manufacture is carried on in various places on the east coast of England and Scotland. It is also carried on to a large extent in London, the raw material being the fish offal of the metropolis, which, for the most part, is simply dried and ground. The principal value of fish guano lies in its nitrogen, which may vary from as little as 6 or 7 p.c., to as much as 10 or 11 p.c. according to the particular kind of fish or fish offal from which it is made, and the presence or absence of much salt or other impurities. There is also a good deal of calcium phosphate, which usually varies inversely with the nitrogen, and may range from as little as 6 or 7 p.c. up to 18 or 20 p.c. The potash is inconsiderable. The following analyses represent different qualities of fish guano :—

ANALYSES OF FISH GUANO.

Moisture . .	14·18	8·78	14·42	11·18
*Organic matter .	54·07	63·92	63·68	67·22
†Phosphoric acid .	5·58	7·85	7·50	7·72
Lime . . .	6·16	10·47	8·06	8·34
Salt, magnesia, potash, &c. .	17·31	7·03	5·54	5·14
Sand . . .	2·70	1·95	0·80	0·40
	100·00	100·00	100·00	100·00
*Containing nitrogen	6·27	8·74	9·62	10·42
Equal to ammonia	7·61	10·61	11·68	12·65
†Calcium phosphate	12·19	17·15	16·39	16·87

The practical value of the manure depends to some extent on the quantity of oil present, the smaller the quantity of oil the more readily does the manure decompose in the soil.

Phosphatic guanos. The ancient deposits of guano occurring in climates in which rain is frequent have lost almost the whole of their nitrogenous matter; they are, when free from sand or rock, of value as phosphatic manures, but have been chiefly used for the manufacture of high-class superphosphates. Some of these guanos have been considerably altered by the action of water and other natural chemical agents. One common result of this action is the formation of 'crusts,' consisting largely of calcium phosphate containing considerably less calcium than tricalcium phosphate, and therefore of special value as manure. Gypsum is also present in some cases to a considerable extent.

The principal places from which phosphatic guanos have been obtained are various islands in the West Indies and in the Pacific Ocean. Those which more particularly retained some of the distinctive characters of guanos are now for the most part used up. More deposits are still occasionally discovered, but in many cases these deposits have become so metamorphosed that they have almost passed the border line between 'guano' and 'mineral phosphate,' which is sometimes not easily drawn. At all events, their function is not that of manure, but of a raw material for its manufacture, and for practical purposes they may be placed with mineral phosphates, to be considered presently.

Ammonium sulphate (commercially called sulphate of ammonia) usually contains from about 95 to 97 p.c. of the pure salt, containing 20–20·5 p.c. of nitrogen, equivalent to from 24 to 25 p.c. of ammonia.

Sodium nitrate (commercially called nitrate of soda) is refined from the crude native deposits (known as caliche), found in the rainless areas of Chile. Good commercial sodium nitrate contains about 95 p.c. of sodium nitrate or 15·6 p.c. of nitrogen (equivalent to 19 p.c. of ammonium). The impurities are moisture, sodium chloride, sodium and magnesium sulphates, small quantities of iodates and sometimes of potassium perchlorate, while in some makes sodium nitrate is partially replaced by potassium nitrate.

Potassium nitrate, or saltpetre, is sometimes used as a source of both nitrogen and potash, but chiefly in India, where it is a native product.

Calcium nitrate has recently been introduced as a fertiliser. Its chief interest at present lies in the fact that it is manufactured from nitric acid produced from the direct combination of atmospheric nitrogen and oxygen in the flaming electric arc. Its production is said to be already considerable, but from an economical standpoint it will assume larger importance in the future, when the present abundant sources of naturally formed nitrate come to an end. As put on the market at present, it contains about 13 p.c. of nitrogen (equivalent to about 15·8 p.c. of ammonium). Its chief fault in its present form is its extreme deliquescence, which makes it necessary to sow it directly the air-tight drums in which it is sent out are opened.

Calcium cyanamide is also a fertiliser made from the nitrogen of atmospheric air: which is passed through coarsely ground heated calcium carbide. The resulting mass contains a large proportion of calcium cyanamide, and contains about 18–20 p.c. of nitrogen. In moist earth it decomposes, yielding ammonia, according to the reaction $CaCN_2+3H_2O=2NH_3+CaCO_3$; but it is probable that other influences than mere moisture—connected probably with the microbic life of the soil—play a part in the production of ammonia. As calcium carbide is a product of the electric furnace, calcium cyanamide, like calcium nitrate, needs electric power for its production. For its manufacture *v.* NITROGEN, ATMOSPHERIC, UTILIZATION OF. It is put on the market under the name of 'kalk-stickstoff' on the Continent, or 'nitrolim' in England.

Some forms of calcium cyanamide, especially of a granulated type made by using excess of lime, contain considerable quantities of dicyandiamide, the action of which appears to be directly deleterious to some crops and to tend to inhibit nitrification in the soil (Voelcker, J. Roy. Agric. Soc. 1917; also Cowie, J. Agric. Sci 1919, vol. 9, part 2).

Oilcakes. Cheap or damaged oilcakes, or cakes unfit for food (as castor), are employed to a considerable extent as manure, and more particularly the residual meals obtained as by-products in the extraction of oil by spirituous solvents from rape seeds, castor-oil seed, and numerous other oil seeds. They are in large request for hop manuring, and for general use on light soils, on which the farmer prefers a less rapidly active form of nitrogen than is furnished by guano, sodium nitrate, or ammonium sulphate. They will contain 4–7 p.c. of nitrogen, 1·5–3·0 p.c. phosphoric anhydride, and 1–2 p.c. potash.

Hoof and horn. The powdered horn obtained in making combs and other articles is used to a considerable extent by manure manufacturers; it is extremely rich in nitrogen, containing about 15 p.c.

Dried blood. This is a very valuable manure, its nitrogenous matter becoming readily available to the crop after mixing with the soil. Perfectly dry blood will contain about 15 p.c. nitrogen and 4 p.c. ash, of which one-half is common salt. The commercial article contains from about 11 p.c. to about 13 p.c. of nitrogen. It is in growing demand for direct application to the soil, but the greater part both of the dried blood manufactured here and of that imported from South America is purchased by the manure makers and incorporated in compound fertilisers.

Meat meal, meat guano. The residue from the manufacture of meat extract is exported as manure from South America, and from Queensland and New Zealand. The composition varies much, chiefly according to the proportion of bone ground up with the meat. The nitrogenous samples may contain 11–13 p.c. nitrogen, and 0·6–3·0 p.c. phosphoric anhydride. The phosphatic samples may contain 6–7 p.c. nitrogen, and 14–17 p.c. phosphoric anhydride.

Shoddy and wool waste. These are useful nitrogenous manures, but much less active than those previously enumerated, being only slowly decomposed in the soil. They are less used than formerly, except for hops and market gardening, owing to the cheapness of ammonium salts. Pure dry wool and hair would contain about 17 p.c. nitrogen, and 2 p.c. ash. The percentage of nitrogen in ordinary shoddy varies from 5 to 8, the general average being about 7. Shoddy is apt to contain a good deal of water; the other impurities are cotton, oil, and mineral dust.

Leather. The percentage of nitrogen is 4–6. This is the least active form of nitrogenous matter used as manure; but there are various manufacturing processes—such as treatment with acids or with steam under high pressure—whereby the character of the leather as such is more or less destroyed, the result being a fine powder capable of undergoing more rapid decomposition, and having, in some cases, a large proportion of actually soluble nitrogen.

Soot. House soot is used by farmers as a top dressing for spring corn. Good soot contains about 4 p.c. of nitrogen or nearly 5 p.c. of ammonia (say 20 p.c. of ammonium sulphate), in which form the nitrogen largely exists, but it often contains an admixture of ashes, and consequently varies a good deal.

Bones. These are seldom used in their fresh state; they have generally been first steamed to extract the fat. A more perfect method of extracting the fat by means of benzene has been introduced (J. Soc. Chem. Ind. 1884, 375, 490, 575), but not much employed. Less nitrogenous matter is removed from the bone when benzene is used. A third form of bone is that left after extracting the greater part of the gelatinous matter by boiling under pressure. The analyses in next column illustrate the composition of bone manures.

Bones are either applied to the land directly as crushed bones, or as bone-dust or bone-flour; or they are employed for the manufacture of 'dissolved bone.' The soft parts of bone are more nitrogenous than the hard parts. Bone-flour is a fine powder, prepared from highly steamed bones.

BONE MEAL.

	English (containing cartilaginous matter)	English (ordinary)	Indian	Boiled or lightly steamed	Steamed or de-gelatinised
Moisture	8·24	8·80	8·48	8·62	13·52
*Organic matter	36·14	34·94	30·56	20·74	9·88
†Phosphoric acid	20·75	21·66	24·19	26·44	30·11
Lime	27·94	28·53	32·03	35·95	40·04
Magnesia, carbonic acid, &c.	5·18	4·62	4·19	7·25	5·45
Silicious matter	1·75	1·45	0·55	1·00	1·00
	100·00	100·00	100·00	100·00	100·00
*Containing nitrogen	4·72	4·19	40·1	2·33	0·91
Equal to ammonia	5·73	5·09	4·87	2·83	1·11
†Equal to tricalcium phosphate	45·31	47·33	52·85	57·77	65·79

Bone ash. This is imported from South America. It was formerly much used for preparing high-class superphosphates, but is now less employed, owing to the abundance of cheaper phosphates. Pure ox bone ash will contain nearly 40 p.c. phosphoric acid. The commercial article is usually sold on a basis of 75 p.c. tricalcium phosphate.

Basic slag. By the process patented by Thomas (1877–79), the phosphorus is removed from pig-iron. The melted iron is placed in a Bessemer converter lined with lime, a large dose of lime is added, and the blast applied. At the high temperature reached, the impurities in the iron are oxidised by the air introduced, the phosphorus becomes phosphorus pentoxide and unites with the lime. A slag is formed containing about 40–50 p.c. lime, varying quantities of magnesia, alumina, iron oxide, manganese oxide, silica, and phosphoric acid equivalent to from 20 to 50 p.c. of tricalcium phosphate. The process has been adopted to a very large extent, and basic slag is now an important product of the iron and steel industry. It has been estimated that at the present time (1910) 300,000 tons are annually produced in Great Britain alone, and the continental production is very heavy.

For several years, however, the slag was regarded as valueless, the large amount of iron present leading agricultural chemists to believe that the phosphoric anhydride would not prove available to plants, while the ferrous oxide would probably be injurious. It is now known that the phosphoric anhydride in the slag is almost wholly combined with calcium, and that this calcium phosphate is easily disintegrated and rendered soluble in the soil, and that no ill effects arise from the presence of the ferrous oxide. Tetracalcium phosphate has been regarded as the combination in which most of the phosphorus occurs (Hilgenstock, Dingl. poly. J. 250, 330; Otto, Zeitsch. Chem. 11, 255; Bücking u. Zinck, Stahl u. Eisen, 7, 245); but it is probable that the phosphate has more nearly the composition $(CaO)_4,P_2O_5,SiO_2$ (Hall). About 1·5 p.c. of the total phosphorus exists as iron phosphide, which is changed into phosphate in the soil (Jensch, Zeitsch. Chem. 10, 820).

The phosphate in the slag is not soluble in water; it is dissolved to a considerable extent by a solution of ammonium citrate, and when the slag is finely ground about 80 p.c. of it should dissolve in a 2 p.c. solution of citric acid.

Much basic slag is also now produced in the open hearth process. This is of lower grade of phosphorus content and of low citric acid solubility owing to the use of calcium fluoride as a flux.

Field experiments with finely ground untreated slag commenced in 1882, and it was found to produce an excellent effect. The Germans were the first to realise the importance of the new manure, and they succeeded in purchasing in advance a large proportion of the English make.

To be effective the slag must be very finely ground; at least 80 p.c. of it should pass through a sieve having 100 meshes to the linear inch. The grinding requires special machinery. It is advisable, according to Horn (J. Soc. Chem. Ind. 1886, 242), to break first under stamps, to further reduce between rollers, then to separate pieces of iron by passing over slanting sieves, and finally to grind between millstones.

According to Wagner's trials, 2 parts of phosphoric acid in powdered slag (of which 80 p.c. passed a sieve with meshes 0·2 mm. diameter) are equal in manuring power to 1 part of soluble phosphoric acid in superphosphate; the effect will, however, vary in different soils.

Basic slag is especially valuable on moorland soils rich in organic matter and on clay soils deficient in lime on which the continuous use of superphosphate is undesirable. It has proved especially valuable on pastureland.

Precipitated phosphate. Phosphatic minerals which are unsuitable for the manufacture of superphosphate, either from their poverty in phosphate or from the presence of an objectionable amount of iron oxide or alumina, are sometimes treated with acid, the calcium phosphate dissolved out, and then recovered by precipitation. If the addition of the neutralising base is stopped while the solution is still acid, the precipitate will consist chiefly of dicalcium phosphate.

The phosphoric anhydride in precipitated phosphate stands next in value to that existing as monocalcium phosphate. Commercial dicalcium phosphate may contain as much as 40 p.c. P_2O_5; it is thus a very concentrated manure, and especially suitable for use where manure must be conveyed a long distance. Owing to the introduction of basic slag, however, it is now scarcely worth while to manufacture precipitated phosphate except as a by-product. It is thus prepared incidentally to the manufacture of gelatin from bones. The bones are treated with cold hydrochloric acid, which dissolves out the phosphate, leaving the chondrin or gelatinoid matter undissolved. The phosphate is then recovered from the acid solution by precipitation with milk of lime.

Superphosphate. The phosphates previously mentioned may be applied directly to the soil with good effect, if in the condition of fine powder. Natural mineral phosphatic deposits are, however, too hard and insoluble to be economically used in this manner; these are treated with sulphuric acid, and converted into superphosphates.

The treatment of bone with sulphuric acid was originally recommended by Liebig. The treatment of mineral phosphates with sulphuric acid originated with Lawes, who took out a patent for this process in 1842, and founded a manufacture which has since reached enormous dimensions.

Superphosphate in the United Kingdom is always sold on the basis of its percentage of what is called 'soluble phosphate.' This means the quantity of tricalcium phosphate which has been rendered soluble. The phosphoric acid (P_2O_5) soluble in water is determined and calculated into its equivalent percentage of $Ca_3P_2O_8$, this being called 'soluble phosphate.' On the continent of Europe the solubility is, on the other hand, calculated as 'soluble phosphoric acid,' *i.e.* P_2O_5 dissolved by water. The method of determination will be described later on.

Phosphatic Materials used.

Superphosphate was prepared by Lawes in the first instance from spent animal charcoal; Suffolk (Tertiary) coprolite and Estremadura phosphorite were also early employed. The Suffolk coprolite was for 15 years the principal material made use of. The far superior Cambridge (Greensand) coprolite then became for many years the chief material, but is now scarcely, if ever, used, other phosphates being much cheaper. Deposits rich in calcium phosphate have been found all over the world; many of these have been exhausted, and others given up as of inferior quality, or as being at present prices too expensive to work. We shall give some account both of some of those which have become matters of history, or the use of which is at present in abeyance from the effect of competition, as well as of those which are at present in use. The estimates given of the quantities of the various phosphates recently mined or raised are taken from a paper read at the International Congress of Applied Chemistry, in 1909, by Hermann Voss, who estimated the total output of raw phosphate in 1908 at the enormous quantity of 4,824,000 tons. This would represent in all something like 8½ million tons of superphosphate.

South Carolina or Charleston phosphate. This is apparently a converted Eocene marl. It occurs in rough masses, largely perforated by boring mollusca, and associated with fossil bones and teeth. It is classed as 'land' and 'river' phosphate; the latter is obtained by dredging the Bull, Coosaw, and Stono rivers. This phosphate came first into use in 1867, and soon became the chief material for the manufacture of superphosphate. The quantity exported to the United Kingdom in 1887 was 165,275 tons (principally river phosphate); in the same year 430,549 tons were used in the United States. There are three grades, containing phosphoric acid equal to 50–52, 55–56, and 58–60 p.c. tricalcium phosphate; they differ simply in the proportion of silicious matter present. South Carolina phosphate, though not rich enough for the preparation of high-class superphosphates, is an admirable material for the production of an ordinary superphosphate, containing, according to the quality of the phosphate used, from 11 to 14 p.c. soluble phosphoric acid, or, in commercial language, 24–30 p.c. soluble phosphate. Owing to the discovery of other deposits and to the local demand for this particular phosphate in the United States, it has at present practically ceased to be imported into England. The quantity of phosphate raised in 1908 in South Carolina and Tennessee is estimated by Voss at 800,000 tons.

Belgian and Somme phosphate. In the north of France (departments Somme and Pas de Calais) and in the adjoining districts of Belgium there exists an enormous deposit of a friable phosphatic rock, 'craie grise,' extending over seven million acres. This deposit lies on ordinary white chalk; it consists of yellowish grains embedded in a chalky matrix. The rock contains 20–30 p.c. of calcium phosphate, occurring in the crystalline grains above mentioned. In the upper layer of this deposit are pockets, chiefly developed in France, which contain a sand far richer in phosphate and poorer in carbonate than the underlying rock, the proportion of phosphate in this sand being 50–80 p.c. The sand has probably been formed from the original rock by the action of water. This phosphatic sand is known as 'Somme phosphate.'

The Belgian phosphatic rock is generally of low quality. By washing and blowing, a material containing 40–45 p.c. calcium phosphate is produced. Many schemes have been tried for removing the calcium carbonate, and thus raising the value of the material; none has yet become a commercial success. Belgian phosphate is used with other phosphates as a diluent; the carbonate it contains produces much gypsum when acted on by the sulphuric acid, and considerably improves the porosity and dryness of the manure. The export from Belgium to the United Kingdom is considerable.

One practical advantage possessed by the Belgian and Somme phosphates is that they require no grinding. Somme phosphate as imported goes entirely through a sieve of 60 wires to the inch. The output of Belgian phosphate in 1908 was estimated at 150,000 tons, and of Somme and other French phosphate at 350,000 tons.

Phosphorites. Large deposits of apatite, or of phosphates having an apatite character, occur in many places; those most worked have been the Estremadura, the Canadian, and the Norwegian. These, however, are not now brought to this country, and have for the present ceased to be worked.

1. *Estremadura phosphorite.*—An immense deposit occurs in Caceres. In composition it is a fluor-apatite, but mixed with much quartz, and with more or less calcium carbonate. There are three qualities, containing about 50, 60, and 70 p.c. tricalcium phosphate. The calcium carbonate varies from 6 to 16 p.c. The exports were in former years very large, amounting sometimes to 60,000 tons per annum.

2. *Canadian phosphorite.*—This is much richer than the Estremadura phosphorite, containing 70–80 p.c. tricalcium phosphate. The lower qualities contain much mica. The amount formerly exported to the United Kingdom was considerable.

Caribbean phosphates. Under this head we group the rock phosphates found on many of the West India Islands, some of which are often classed as phosphatic guanos.

1. *Aruba.*—This is one of the Dutch islands. The phosphate is of high quality, containing 75–80 p.c. tricalcium phosphate, but the imports now are small. The total quantity raised in 1908 is estimated at 30,000 tons.

2. *Curaçao.*—Another Dutch island. This, which is now being largely worked, is one of the finest phosphates available, containing about 85 p.c. tricalcium phosphate. With this phosphate, superphosphate may be made containing 44–45 p.c. soluble phosphate (20–20½ p.c. soluble P_2O_5).

3. *Sombrero.*—This valuable deposit is nearly exhausted. It contains 70–78 p.c. tricalcium phosphate.

4. *Monk and St. Martin's Islands.*—Both deposits are now exhausted; the former was of very high quality.

5. *Navassa.*—The deposit on this island has a well-marked pisolitic structure. The phosphoric anhydride is equivalent to 60–70 p.c. tricalcium phosphate. The use of Navassa phosphate is limited by the considerable amount of alumina and ferric oxide present, which makes it unsuitable for the preparation of high-class superphosphates.

6. *Redonda and Alta Vela.*—The phosphates of these islands consist chiefly of aluminium phosphate. They are quite unsuitable for the manufacture of superphosphate. They have been dissolved in sulphuric acid, and the alumina separated as alum. It has also been found possible to obtain a large proportion of the phosphoric acid as sodium phosphate by heating with sodium chloride in superheated steam, or by firing with sodium sulphate and carbon (J. Soc. Chem. Ind. 1886, 570).

Bordeaux phosphate. Raised in the departments of Lot and Tarn-et-Garonne. This is now little used in England, as it is not rich in phosphate, and contains a good deal of ferric oxide and alumina.

Nassau or Lahn phosphate. This is still used locally, but the exports to this country have ceased. It varies much in composition; the higher qualities are suitable for the manufacture of superphosphate, but the lower qualities contain much iron. This phosphate is remarkable as containing a distinct amount of iodine.

Coprolites. The phosphatic nodules commonly known as coprolites, found in England, are scarcely used now, cheaper phosphates being available. The Cambridge (Upper Greensand) coprolite was the best of the English sorts; it contained 55–60 p.c. tricalcium phosphate, without an admixture of ingredients prejudicial to the production of soluble phosphate. The Suffolk coprolite (Tertiary) contains less phosphate (55 p.c.), and more ferric oxide. The Bedfordshire coprolite (Lower Greensand) is still more inferior, the ferric oxide being present in increased proportion.

In France there are considerable deposits of coprolite in the Upper Greensand in the departments of Pas de Calais, Meuse, and Ardennes; those from Pas de Calais are shipped to England from Boulogne. These coprolites generally contain a low proportion of phosphate, and much silicious matter.

Florida phosphate. Extensive deposits of high-grade phosphate have been opened up during recent years in the State of Florida. The phosphate is of two kinds, namely, 'hard rock' phosphate and 'pebble' phosphate. The rock phosphate commonly contains from 78 to 80 p.c. of tricalcium phosphate, and the pebble phosphate about 70–74 p.c. There is, however, also a high-grade pebble phosphate containing from 78 to 79 p.c. of tricalcium phosphate. These phosphates are very widely used in superphosphate. According to the estimates of Voss, 600,000 tons of Florida 'hard rock' phosphate and 900,000 tons of Florida 'pebble' phosphate were raised during 1908.

African phosphate. An extensive range of phosphate deposits is now worked on or near the northern coast of Africa, known in commerce as Algerian, Tunisian, Tocqueville, Gafsa and Egyptian phosphates. These are soft, powdery, or friable minerals, containing for the most part comparatively little silicious matter, but a large proportion of calcium carbonate. The proportion of tricalcium phosphate is commonly somewhere near 60 p.c., varying from about 59 p.c. to nearly 64 p.c. The quantities of North African phosphates mined in 1908 were estimated by Voss at over 1,500,000 tons. Some of them are now prepared in a finely ground state for direct application to the soil.

Christmas Island phosphate. This is a deposit found on Christmas Island—an island lying in the Indian Ocean south of Java. It contains about 87 p.c. of tricalcium phosphate, and makes excellent superphosphate. At present the output is said to be largely consumed in the manufacture of superphosphate in Japan.

Pacific phosphate. Valuable deposits of similar high-grade phosphates, containing 86 or 87 p.c. of tricalcium phosphate, accompanied by very little ferric oxide or alumina and practically no silica, have been discovered in recent years on certain islands in the Pacific Ocean lying to the north-east of Australia. The principal deposits at present worked are those of Ocean Island and Nauru Island, but deposits have also been found on the islands of Makatea, Tahiti, and Angaur. Much of the phosphate raised on these islands is consumed for superphosphate making in Australia, New Zealand, and Japan. These phosphates in a finely ground state are also now sold for direct application to the soil.

Manufacture of superphosphate. The raw phosphate is first reduced to an extremely fine powder. Considerable improvements have now been effected both in the economy of the grinding and in the degree of fineness attained. If the material is in large lumps, it is first reduced by means of a crusher, and is then transferred to a suitable mill. The Kent mill is largely used for this purpose, and is worked in conjunction with a screen and elevator. The finer the powder obtained, the more complete will be the decomposition by the sulphuric acid. For first-class work the powder should pass through a sieve of 80 wires to the inch. In view of the stringency of modern factory legislation, a dust-collecting plant of some sort, such as the Beth filter, is usually considered necessary in the part of the works devoted to milling.

It has been assumed in some text-books that the reaction in superphosphate making is simply:

$$Ca_3P_2O_8+2H_2SO_4=CaH_4P_2O_8+2CaSO_4$$

This is true as regards the major portion of the phosphate rendered soluble. But in practice, as was first pointed out by Ruffle (J. Soc. Chem. Ind. 1887, 327), the reaction, as regards an appreciable portion of the phosphate, almost invariably proceeds further, thus:

$$Ca_3P_2O_8+3H_2SO_4=2H_3PO_4+3CaSO_4$$

so that a water solution of superphosphate contains a major proportion of $CaH_4P_2O_8$, with a minor proportion of free phosphoric acid H_3PO_4. Indeed, unless there is a fair proportion of the latter, the proportion of 'soluble' phosphate is unstable, owing to liability to reversion by subsequent interaction between the dissolved phosphate and that which was originally left undissolved. Thus well-made superphosphate, when freshly made, often contains as much as from 6 to 10 p.c. of H_3PO_4, and sometimes more.

PERCENTAGE COMPOSITION OF MINERAL PHOSPHATES EMPLOYED IN THE MANUFACTURE OF SUPERPHOSPHATE.

FLORIDA PHOSPHATES. (Dried at 100°.)

—	Hard rock			Pebble, medium grade				Pebble, high grade	
*Phosphoric acid (P_2O_5)	36·05	36·44	36·81	31·92	32·24	32·80	33·98	36·24	35·90
Lime	51·29	50·46	50·96	46·76	46·78	47·18	48·03	49·44	48·68
Alumina	1·42	1·44	1·41	1·28	1·29	1·32	1·23	1·32	9·20
Ferric oxide (exclusive of any pyrites)	0·60	0·60	0·55	1·45	1·50	1·85	1·05	0·60	
Magnesia, carbonic acid, fluorine, &c.	7·84	6·31	6·67	11·66	10·43	9·50	9·46	6·40	
Silicious matter	2·80	4·75	3·60	6·93	7·76	7·35	6·25	6·00	6·22
	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00
*Equal to tricalcium phosphate	78·77	79·62	80·43	69·75	70·44	71·67	74·25	79·18	78·44
Excess of lime over tricalcium phosphate	8·57	7·28	7·34	8·03	8·58	8·31	7·76	6·50	6·14
Moisture in phosphate as imported	0·66	1·60	—	2·11	1·94	2·03	2·33	—	—

NORTH AFRICAN PHOSPHATES.
(Dried at 100°.)

	Algerian		Tocqueville	Tunisian		Gafsa
*Phosphoric acid (P_2O_5) .	27·05	29·04	25·26	27·21	28·44	27·12
Lime	47·79	50·46	43·01	48·83	49·92	44·87
Alumina	0·56	0·44	0·52	0·54	0·48	0·96
Ferric oxide (exclusive of any pyrites) . .	0·25	0·30	0·48	0·30	0·25	0·40
Magnesia, carbonic acid, fluorine, &c. . . .	18·95	16·96	17·33	17·66	17·41	18·95
Silicious matter . .	5·40	2·80	13·40	5·46	3·50	7·70
	100·00	100·00	100·00	100·00	100·00	100·00
*Equal to tricalcium phosphate	59·10	63·45	55·19	59·45	62·14	59·26
Excess of lime over tricalcium phosphate . . .	15·74	16·05	13·08	16·59	16·22	12·73
Moisture in phosphate as imported . . .	—	—	—	3·30	3·24	—

VARIOUS PHOSPHATES.
(Dried at 100°.)

	Christmas Island	Ocean-Nauru	Tennessee	Belgian	French	Canadian	
						Rich	Poor
*Phosphoric acid (P_2O_5) .	39·85	39·84	36·92	19·57	23·80	39·32	29·99
Lime	52·24	53·05	50·59	49·34	52·96	54·18	42·25
Alumina . . .	1·35	0·30	1·59	0·43	1·44	0·40	2·84
Ferric oxide (exclusive of any pyrites) . .	0·45	0·23	1·70	0·65	0·60	0·55	2·03
Magnesia, carbonic acid, fluorine, &c. . .	5·96	6·48	7·46	26·23	20·60	4·11	9·27
Silicious matter . .	0·15	0·10	1·74	3·78	0·60	1·44	13·62
	100·00	100·00	100·00	100·00	100·00	100·00	100·00
*Equal to tricalcium phosphate . . .	87·07	87·05	80·60	42·76	52·00	85·84	65·47
Excess of lime over tricalcium phosphate .	5·02	5·84	6·91	26·15	24·76	7·66	6·77
Moisture in phosphate as imported . . .	1·54	2·52	1·21	0·45	--	—	4·86

	Spanish		West Indian		Coprolites		South Carolina
	High grade	Poor	Aruba	Curaçao	Bedfordshire	Suffolk	
*Phosphoric acid (P_2O_5) .	35·01	25·77	33·63	32·73	25·97	26·30	26·73
Lime	48·49	34·58	48·33	47·29	40·66	41·72	43·62
Alumina . . .	1·79	7·10	1·63	0·35	1·48	22·90	0·83
Ferric oxide (exclusive of any pyrites) . .	1·05		1·75	0·75	5·30		1·45
Magnesia, carbonic acid, fluorine, &c. . .	7·98		12·10	18·38	14·03		17·77
Silicious matter . .	5·68	32·55	2·56	0·50	12·56	9·08	9·60
	100·00	100·00	100·00	100·00	100·00	100·00	100·00
*Equal to tricalcium phosphate . . .	76·43	56·26	73·48	71·45	56·69	57·42	58·35
Excess of lime over tricalcium phosphate .	7·07	4·09	8·48	8·57	9·94	10·60	12·00
Moisture in phosphate as imported . . .	—	1·17	3·04	—	0·65	1·41	0·90

In the first stage of the reaction, phosphoric acid alone is probably produced, and this afterwards reacts on the remaining undecomposed phosphate. The proportion of free phosphoric acid in the resulting manure is greater when strong sulphuric acid has been employed, the total soluble phosphoric acid being, at the same time, diminished. When superphosphates are dried at 100°, a loss of soluble phosphoric acid also occurs, and this loss becomes much greater when a higher temperature is employed (Ruffle). Monocalcium phosphate can, in fact, exist only when in union with water.

A further reaction which is of great practical moment to the manufacturer of superphosphate is the disappearance of soluble phosphate by keeping. The regenerated insoluble phosphate is known as 'reverted phosphate.' This deterioration during storage is not observed in the case of well-made superphosphate prepared from finely ground mineral phosphate containing no appreciable quantity of iron or aluminium, but it is observed when ferric oxide or alumina is present.

So long as superphosphate is valued on the basis of its contents in soluble phosphate, ferruginous and aluminous phosphates will be avoided by the manufacturer. On the Continent, however, and in the United States, reverted phosphate has a considerable money value, and mineral phosphates containing iron and aluminium consequently find employment.

The sulphuric acid employed is usually pyrites-made chamber acid of 1·55 to 1·60 sp gr. Weak acid is essential, as the dryness of the superphosphate depends largely upon sufficient water being present for the crystallisation of the calcium sulphate ($CaSO_4.2H_2O$) formed by the reaction. It follows that, when much calcium carbonate is present in the phosphate, weaker acid will be required than when but little calcium carbonate is present. When calcium fluoride is present in considerable quantity, and very little or no calcium carbonate (as in apatite), acid stronger even than 1·60 sp.gr. is necessary, as calcium fluoride is not so readily decomposed as calcium carbonate.

The proportion of sulphuric acid to be used depends, of course, upon the composition of the phosphatic material. Theoretically, 100 of tricalcium phosphate will require 94 of sulphuric acid of sp.gr. 1·60 (55 p.c. SO_3), or 100 of sulphuric acid of sp.gr. 1·55 (51·5 p.c. SO_3), if monocalcium phosphate is to be produced. The proportion of sulphuric acid used in practice is usually as large as can be employed without endangering the dryness of the product. It is generally somewhat in excess of that needed to produce monocalcium phosphate, but is considerably below that required to yield only phosphoric acid. For South Carolina river phosphate, the ordinary proportion is 95 p.c. of sulphuric acid of sp.gr. 1·57.

The excess of lime present in the material (as carbonate or fluoride) is a principal factor in determining the quantity of sulphuric acid to be employed: 100 of lime will require 260 of acid sp.gr. 1·6 or 277 of acid sp.gr. 1·55 to produce calcium sulphate. At the foot of the table previously given will be found the excess of lime (over that required to form tricalcium phosphate) present in each of the mineral phosphates commonly employed. Phosphates containing a considerable excess of lime will yield a poorer superphosphate than their percentage of phosphoric acid would seem to warrant, owing to the large proportion of sulphuric acid which they require.

To prepare a 'mineral superphosphate,' the only ingredients are the powdered phosphate and sulphuric acid. When turnip manures, or other manures containing a little nitrogen, are prepared, crushed bones, powdered hoof and horn, shoddy, or ammonium salts, are added when the ingredients are mixed. Mixed superphosphates, formerly called 'dissolved bones,' are usually prepared from a mixture of mineral phosphate, bone, and some concentrated nitrogenous matter.

Owing to the requirements of the Fertilisers and Feeding Stuffs Act, however, such mixtures are now sold as 'dissolved bone compounds,' the term 'dissolved bone' or 'vitriolised bone' being restricted to fertilisers made from pure bone and acid only. Usually, in such cases, only from one-half to two-thirds of the phosphate is actually soluble in water, but much of the remainder is in the readily assimilable form of dicalcium dihydrogen phosphate. If enough acid were used to dissolve all the phosphate, the product would be too pasty for sowing.

The mixer in which the reaction takes place stands on a platform, over an empty chamber, variously known as the 'bin,' 'den,' or 'pit.' It consists of a cylinder, sometimes nearly horizontal, sometimes vertical, furnished in the centre with a revolving shaft, carrying arms set on screw-wise. Into this mixer the charge of weighed 'dust' is emptied, bag by bag, while, at the same time, a measured quantity of sulphuric acid is run in from a tank. When the charge is completed, agitation is continued for two minutes; a valve is then opened, and the whole contents of the mixer (about 16 cwt.) allowed to fall into the pit below. Ten charges can be easily worked in one hour. The pit below is built of brick or concrete on three sides, the fourth side consists of a wooden hoarding which is taken down when the pit is being emptied. A pit will hold from 80 to 140 tons. The fluid material which enters the pit rapidly reaches a temperature considerably exceeding 100°, and then becomes solid. In a few hours it is ready to be excavated.

Formerly the excavation of the super-phosphate was accomplished by the simple means of digging it out by the aid of pickaxes. At the present time, however, manual labour is being gradually superseded by the use of mechanical appliances, many patents for inventions for doing this part of the work having been taken out. Among these, one of the best known is the superphosphate excavator of Dr. A. Keller, of the Anglo-Continental Guano Works of London, Hamburg, Antwerp, and Düsseldorf, which is now in successful use in various parts of the world. This machine consists of an arm extending from a staging, which latter travels upon metals laid in front of the pit; the arm is furnished with travelling knives and scrapers, and it revolves on a pivot around the staging as a centre, so that it can be swung in and out of the pit and be made to reach to the extreme back part of it. When the knives and scrapers are set in motion, the superphosphate is scraped forward and dropped on to a conveyor traversing the front of the pit, whence it can be elevated and conveyed to the part of the works where it is required to be stored. The machine is so constructed that the arm is made to move from left to right and *vice versâ*, and lower itself automatically as the superphosphate is removed.

The gases given off during the reaction, both from the mixer and pit, are of a particularly unpleasant description, especially when the phosphate contains fluorides. Both mixer and pit are provided with flues in connection with a fan, by which all the gases are removed; these are purified in a scrubber, and then conducted to a tall chimney.

Well-made superphosphate is a porous mass, the cavities being due to imprisoned gas. It is usual to break up the lumps at the time of manufacture by passing it through a rotary screen, and to further grind and screen it after storing and before delivery. If mixed manures are to be made, the other ingredients are added while passing through the disintegrator.

By adding ammonium sulphate or other nitrogenous material, with or without potash salts, 'corn,' 'grass,' 'mangel,' and 'potato' manures are produced. Sodium nitrate cannot safely be added to superphosphate unless the latter is very dry; if this precaution is neglected, free nitric acid is produced, the manure bags are destroyed, and serious mischief may occur. To employ ammonium sulphate and sodium nitrate together is still more objectionable, as ammonium nitrate is formed, and even when it does not suffer decomposition it ruins the manure by its deliquescence.

Ordinary superphosphate is made from a mixture of phosphates, and contains 26 p.c. of dissolved phosphate (=11·9 p.c. P_2O_5) and 2–3 p.c. of undissolved phosphate. The turnip manures containing bone have generally rather less of dissolved phosphate, more of undissolved, and nearly 1 p.c. of nitrogen. Special manures of greater strength are also prepared. From high-class phosphate, superphosphate containing 30–31 p.c. dissolved phosphate (13·7–14·2 P_2O_5) may be obtained. High-grade Florida rock will yield superphosphate containing 38–39 p.c. dissolved phosphate (17·4–17·9 P_2O_5). From Ocean Island and Christmas Island phosphates, superphosphate with 44–45 p.c. dissolved phosphate (20·2–20·6 P_2O_5) may be prepared.

Far richer superphosphates are obtained by the process patented by Packard (Eng. Pats. 6178, 6750, 6752). Superphosphate, prepared so as to be rich in free phosphoric acid, is extracted with water, the solution evaporated to sp.gr 1·125–1·300, and sufficient calcium phosphate, carbonate, or hydroxide added to leave one-third of the phosphoric acid in the free state. The solution is then filtered, and the filtrate evaporated to dryness. The product contains about 40 p.c. of soluble phosphoric acid, equal to 87 p.c. of so-called 'soluble phosphate.' This superphosphate has a special value where manure has to be conveyed a long distance.

There is a large export trade in English-made superphosphate.

Gypsum. This has in most cases a very small value as a manure. Where superphosphate is employed, it is applied in this manure. Massive gypsum is imported from the South of France. It was formerly used as a diluent in making the lower class of superphosphates, but its place is now taken by Belgian phosphate. It is an excellent drier for mixing with damp manure.

Lime, chalk, and marl. These can hardly be classed as artificial manures, as they are not generally applied as plant foods, but for the sake of the considerable amelioration of the soil which they effect.

Potassium salts. These will be found described under their own head.

THE RELATIVE VALUE OF MANURES.

We have described as briefly as possible the various nitrogenous and phosphatic manures at present used. The important question remains, Have the nitrogen and phosphoric acid the same value in all these manures? and, if not, what is the difference of value? This question may be considered from (1) a trade point of view, viz. by calculating from the market price of various manures what is the money value of their chief constituents. If the prices given for manures were determined by an accurate knowledge of their effect in the field, these prices would really show us their average relative value. As a fact, market prices do generally indicate, though sometimes very imperfectly, the relative manuring value of different manures. The matter may also be considered from (2) the data afforded by actual investigation. In this case, we soon find that the number of available investigations is insufficient, and that the relative value of the same manures differs more or less with differences in the soil, crop, and season. Certain points, however, are fairly well established.

Nitrates are, in a large majority of cases, the most active, and therefore the most valuable, form of nitrogen. Comparisons between sodium nitrate and ammonium salts, containing similar amounts of nitrogen, have been made for many years at Rothamsted, and also at Woburn. With cereal crops the nitrate, on an average, yields distinctly more corn and considerably more straw than the ammonia. The produce by the nitrate is most in excess in dry seasons; in a wet season the ammonia may be superior. On pasture, the relative superiority of the nitrate is about the same as with cereals. With potatoes, ammonia, apparently, is equal to nitrate. With mangel-wurzel, or sugar beet, the nitrate is far superior. A good result with ammonium salts is much more dependent on the presence of abundance of phosphates and potash in the soil than is the case with nitrates. Nitrates and ammonium salts, in favourable circumstances, give all their effect in the first year of their application.

Cyanamide, under favourable conditions, gives results similar to those obtained from a corresponding quantity of ammonium sulphate, but its action depends upon its time of application and upon suitable weather, and probably upon the texture and composition of the soil, as well as on biological considerations. It is best used after admixture with superphosphate, though it has the incidental effect of 'precipitating' soluble phosphate. It is not a pleasant substance to handle in its raw condition, and, if sown alone, it should be sown by means of a mechanical distributor.

The effect of organic nitrogenous manures differs in different soils. In a clay soil, bones decompose so slowly as to be of little value. Organic manures, as shoddy, oilcake, bones, and farmyard manure, yield only a small portion of their nitrogen to the crop during the first year, and several years will elapse before the supply is exhausted. The continued use of such manures increases the proportion of nitrogen in the soil. The proportion of the nitrogen in the manure that is recovered in the crop is frequently smaller than that obtained under favourable circumstances in one season from the application of sodium nitrate, the slowly acting manures being, in the case of arable land, subject to an annual loss of nitrogen as nitrates by drainage. Organic nitrogenous manures are more active in proportion as they are finely divided, and when applied to a well-aërated soil. They are best applied in autumn, while nitrates and ammonium salts should be applied in spring.

Pot culture experiments have been made by Wagner on various nitrogenous manures. If the crop yield obtained from sodium nitrate be represented by 100, the relative efficacy of a like quantity of nitrogen supplied in other fertilisers proved to be as follows:—

Sodium nitrate	100
Ammonium salts	94
Peruvian guano	87
Green plants	77
Horn meal	74
Dried blood	73
Castor cake	73
Wool-dust	26
Cow manure	22
Leather meal	16

But it does not necessarily follow that these figures represent the relative value of the fertiliser in all the varied conditions of practical farming. This subject is being investigated by field trials at Rothamsted.

The relative value of different forms of phosphates has been a subject of much controversy. Some mineral phosphates (as apatite) having been found almost useless as manure, it was too hastily concluded that (with the exception of bone and guano phosphates), only phosphates soluble in water were effective. It has been maintained that very fine grinding will render any phosphate as available as soluble phosphate.

In considering the subject we should bear in mind that the phosphates in the soil, on which plants feed, are not soluble in water, drainage waters being free from phosphoric acid. Soluble phosphate when applied to a fertile soil is quickly precipitated, and is generally finally converted into a hydrated ferric or aluminium phosphate. The practically insoluble phosphates of the soil are dissolved by the acid sap of the root hairs immediately before absorption by a crop or by the carbonic-acid-laden water of the soil.

One great advantage possessed by a phosphate soluble in water consists in its diffusibility. When rain falls after an application of superphosphate, the phosphoric acid is distributed in the soil more perfectly than can be achieved by any other mode of application, and consequently a greater number of root hairs may come in contact with it. Superphosphate is thus more immediately effective than any other form of phosphate. The superiority of superphosphate is, however, not shown in the case of some soils very poor in lime, and in which any additional supply of acid matter is hurtful to the plant; in such cases an assimilable undissolved phosphate may produce a better result.

In view of this, an article known as 'basic superphosphate' is, on the suggestion of Mr. John Hughes, sent out by various manufacturers. It consists of superphosphate neutralised by admixture with sufficient lime to convert the originally soluble phosphate into 'precipitated' or 'reverted' phosphate.

On such soils (poor in lime), basic slag, Peruvian guano, or fine bone meal, also find an appropriate place.

Numerous experiments have been made regarding the assimilability of mineral phosphates when finely ground. It appears that apatites and other crystalline phosphates not disintegrated in the soil, have a very small effect as manure even when finely ground. The small crystalline grains of the Somme phosphate lie in this category. The majority of mineral phosphates are, however, effective as manure when very finely ground, but to a different extent on different soils. The conditions favourable to the use of undissolved phosphates are presence of humus and absence of lime. On the moor soils of Germany, where such conditions prevail, basic slag has had its greatest success. A calcareous soil is the one most unsuitable for the use of undissolved phosphates, calcium carbonate offering a great resistance to the solution of calcium phosphate (Chem. Soc. Trans. 1866, 313).

It is generally admitted that precipitated dicalcium phosphate is nearly equal in effect to soluble phosphate. Phosphates that are soluble in ammonium citrate (including the reverted phosphate of superphosphate) may be safely regarded as assimilable by plants; in America they are regarded as of about equal value with water-soluble phosphate: that they are so always is certainly open to doubt. Phosphates that are insoluble in ammonium citrate are often effective as manure. Ammonium citrate gives thus no safe distinction between assimilable and non-assimilable phosphates, though it affords a useful approximate means of determining 'reverted' phosphate in superphosphate.

As a measure of ready availability in basic slag, a 2 p.c. solution of citric acid has now superseded ammonium citrate.

SPECIAL METHODS OF ANALYSIS.

The enormous quantity of artificial manures bought and sold upon the results of analysis has led to great attention being paid to the question of accurate and speedy analytical methods. To enter into a discussion of all the methods which have been suggested, or even of those which have been 'officially' recognised by the associations of agricultural analysts in different countries, is here impossible.

In the analysis of fertilisers, the object is sometimes merely the determination of a definite fact, such as the percentage of total nitrogen or the percentage of total phosphoric acid. In such cases there are divers processes serving to arrive at the same results. Sometimes, however, the analysis is needed for such a purpose as the determinations of 'soluble' phosphate. Here much depends upon the interpretation of the word 'soluble,' since solubility depends not merely on the nature of the solvent, but upon its proportion to the material acted upon and the mode and duration of its application. It is therefore necessary to define 'solubility' before determining it. Unfortunately, different interpretations of solubility have been in vogue in different countries, causing occasional confusion in international trade, but recent efforts to arrive at international agreement have been attended with some measure of success.

ANALYSIS OF RAW MINERAL PHOSPHATES

Determination of phosphoric acid. The phosphoric acid in mineral phosphates may be accurately determined either by the use of molybdic acid or by what is sometimes called the citric-oxalic-magnesium process, without the intervention of molybdic acid.

There are several modifications of the molybdate process which give fairly accurate and therefore concordant results in the hands of careful workers. Their one common disadvantage is that the quantity of sample represented in the portion of solution finally worked upon is necessarily smaller than in the alternative procedure, and consequently any errors due to inaccuracy of calibration of flasks or pipettes or to lack of exactness in using them, are correspondingly multiplied; and the same observation obviously attaches to errors incidental to the washing of precipitates, the efficiency of filters, and the operations of weighing. There is cogent reason for supposing that many disagreements sometimes attributed to the use of alternative processes are due to insufficient appreciation of some of these sources of error, or to the non observance of the precautions necessary to avoid them. Considerations of the pecuniary cost of molybdic acid sometimes afford a temptation to operate on far too small a scale, and this temptation should be resisted. Thus, many continental analysts were for years content to operate on as little as 0·2 gram of raw phosphate. In such a case, a single milligram of magnesium pyrophosphate (the form in which the phosphate is weighed) is equivalent to approximately 0·7 p.c. of tricalcium phosphate—a grave consideration in the case of large cargoes, the price of which is exactly adjusted to the results of analysis, even to the second place of decimals.

Two modifications of the molybdic process as applied to the analysis of raw mineral phosphates may be given, the first being that of G. Jörgensen, who has devoted much time and attention to the matter, the other that communicated by Dr. M. Ullmann, on behalf of the Verein Deutscher Dunger-Fabrikanten, to the International Congress of Applied Chemistry in London in 1909. Jörgensen's process was originally published in Denmark, but an account of it, communicated by himself, is published in the Analyst, 1909, 34, 392. As there are some differences of detail between the processes, both of which yield accurate results, they may be given side by side. It will be seen that Jörgensen operates finally on a quantity corresponding to 1 gram of the original material, whilst in Ullmann's process the quantity is halved. 1 gram can, however, be equally well taken by doubling the quantity of reagents.

Reagents used.

Solvent.

Jörgensen.	Ullmann.
Nitric acid of sp.gr. 1·21.	*Aqua regia* (3 parts hydrochloric acid of sp.gr. 1·12, and 1 part nitric acid of sp.gr. 1·2).

Molybdic Solution.

100 grams of ammonium molybdate are dissolved in 280 c.c. of ammonia of sp.gr. 0·97, and 300 c.c. of this solution poured with vigorous shaking into 700 c.c. of nitric acid of sp.gr. 1·21, the mixture being allowed to stand for 24 hours.	150 grams of ammonium molybdate are dissolved in 500 c.c. of water. This solution and a separate solution of 400 grams of ammonium nitrate are mixed and made up to 1 litre. The mixture is poured into 1 litre of nitric acid of sp.gr. 1·2, and allowed to stand for 12 hours at 60°, or for 24 hours at the ordinary temperature.

Wash Fluid for Molybdic Precipitate.

40 grams of ammonium nitrate and 10 grams of nitric acid per litre. The author prepares this by mixing 90 c.c. of nitric acid of sp.gr. 1·4 with about 1500 c.c. of water, adding 80 c.c. of ammonia of sp.gr. 0·91 and making up to 2 litres.	32 grams of nitric acid of sp.gr. 1·2 and 50 grams of ammonium nitrate, made up to 1 litre.

Magnesia Mixture.

50 grams of pure crystallised magnesium chloride and 150 grams of pure ammonium chloride, dissolved and made up to 1 litre.	50 grams of pure crystallised magnesium chloride and 150 grams of pure ammonium chloride, dissolved and made up to 1 litre.

Wash Fluid for Ammonium-Magnesium Precipitate.

Ammonia solution containing 2½ p.c. NH_3. (This may be made by diluting 100 parts of ammonia of sp.gr. 0·91 with water to 1 litre.)	Ammonia solution containing 2½ p.c. NH_3.

Method of Jörgensen. Five grams of the mineral phosphate are dissolved in 20 c.c. of nitric acid in a 250 c.c. flask. After gentle boiling for 15 minutes, the contents of the flask are cooled, made up to 250 c.c., and filtered. To 50 c.c. of the filtrate (= 1 gram of the phosphate) in a beaker-flask, 165 c.c. of the molybdic solution are added, and the flask and its contents placed in a water-bath at a temperature of 50° for 10 minutes, with occasional stirring. After cooling and standing, the supernatant liquid is poured through a filter and the precipitate is washed 10 times by decantation with the acid ammonium nitrate solution, about 20 c.c. being used for each washing. The filtrate should be tested with more molybdic solution to see that the precipitation is complete. The washed precipitate is dissolved in 100 c.c. of 2½ p.c. ammonia solution, and filtered, if necessary, through the filter which served for its separation, the filter being washed 8 times with ammonia solution, until the final volume is about 180 c.c. The beaker-flask is covered with a clock-glass, the contents brought just to boiling-point, and 30 to 35 c.c. of the magnesia mixture added drop by drop from a burette, the whole being well stirred and allowed to cool with frequent stirring as long as it remains. If the precipitate is not compact and crystalline, the stirring during this time should be continuous. After standing for at least 4 hours, the precipitate is filtered off, using a platinum (Gooch) crucible packed with spongy platinum, and washed with the 2½ p.c. ammonia solution until free from chlorides, and once with alcohol. It is then dried, heated (at first gently), and then ignited strongly, cooled, and weighed as $Mg_2P_2O_7$.

Method of Ullmann. To 5 grams of the phosphate in a 500 c.c. flask, 50 c.c. of *aqua regia* are added, the whole being evaporated nearly to the consistency of syrup for the elimination of silica. The residue, after setting to an approximately solid mass, is taken up with 10 c.c. of nitric acid (of sp.gr. 1·2) and 50 c.c. of water, boiled, cooled, made up to 500 c.c. with water, and filtered. 50 c.c. of the filtrate (=0·5 gram of the phosphate) are treated with an excess of molybdic solution (at least 100 c.c. for every 0·1 gram of P_2O_5), and digested in a water-bath at 50° for 1 hour. After sufficient standing, the supernatant liquid is poured through a small close filter, and the precipitate washed repeatedly by decantation until free from calcium. At least five washings with 20 c.c. each time are recommended. The filtrate should be tested with molybdic solution to see that the precipitation has been complete. The precipitate is dissolved with from 80 to 100 c.c. of the 2½ p.c. ammonia solution, and filtered through the same filter which served for its separation. The filter should then be washed five or six times with hot water, until the total volume of the solution is from 130 to 150 c.c. The solution is warmed to 60° or 80°, and immediately precipitated with 20 c.c. (or a sufficiency) of the neutral magnesia mixture, added drop by drop with constant stirring. After at least 4 hours' standing, followed by half an hour's stirring, the precipitate is allowed to rest, filtered, and washed with 2½ p.c. ammonia solution until the washings are free from chlorine. The precipitate is dried, gently heated, ignited to constancy, and weighed as $Mg_2P_2O_7$.

CITRIC-OXALIC-MAGNESIUM PROCESS.

The phosphoric acid (and incidentally the lime) may be correctly determined in the following way. Two grams of the mineral phosphate are treated with 25 c.c. of strong hydrochloric acid in a beaker covered with a clock-glass to avoid loss by spraying. After a few minutes' warming, the clock-glass is washed back into the beaker and removed, the beaker being placed in a water-bath and the contents evaporated to dryness. This results in the elimination from solution of not only silica, but of fluorine compounds, the removal of which is essential to the accuracy of the process. Mere evaporation to dryness with a small quantity of hydrochloric acid is insufficient to ensure this removal. It is necessary to use at least the large quantity of acid specified (25 c.c.), so that its evaporation may extend over several hours. (The non-observance of this precaution is a fruitful source of error, resulting in the subsequent formation of magnesium fluosilicate and consequent over estimation of phosphoric acid.) The dry residue is taken up with 5 or 10 c.c. of hydrochloric acid and about 20 c.c. of water, and warmed. The silica, together with pyrites or other insoluble matters, is filtered off and thoroughly washed. To the filtrate and washings (measuring about 150 c.c.), 4 grams of powdered citric acid are added and 3 to 4 grams of powdered ammonium oxalate. The solution is heated nearly to boiling, and rendered just alkaline with dilute ammonia (sp.gr. about 0·970) and excess of acetic acid is immediately added and the liquid is boiled for a few moments. The calcium oxalate is immediately filtered off and washed several times with boiling water, dried, and ignited over a yellow argand flame, and weighed as $CaCO_3$. The precipitate contains all the calcium. It may contain very minute quantities of ferric oxide, aluminium oxide, or manganese oxide, and a minute quantity of phosphoric acid. On this account the precipitate, after being weighed, is dissolved in dilute hydrochloric acid, the solution being boiled and treated with a slight excess of recently diluted ammonia. The small precipitate which forms is filtered through a small filter, washed, and redissolved in a little dilute acid, the solution being boiled and again treated with a slight excess of ammonia. The precipitate is washed, ignited, and weighed. If this small precipitate weighs only 5 or 6 milligrams or less (as is usually the case in the hands of a practised worker), it may be assumed that the precipitate contains P_2O_5 equal to half its own weight of $Mg_2P_2O_7$, this assumption being based on the analysis of a large number of such precipitates. But if, owing to unskilful work or to any peculiarity in the mineral under investigation, the quantity is greater, the little precipitate may be redissolved in hydrochloric acid, with the addition of about 0·1 gram of citric acid, and its solution added to the original filtrate from the calcium oxalate precipitate.

This filtrate is made strongly ammoniacal and the phosphoric acid precipitated by the gradual addition of magnesium mixture, a large excess being finally added. The gradual addition and vigorous stirring are both necessary to ensure that the precipitate comes down in a compact crystalline form. The whole bulk at this stage will be about 350 c.c. After 2 to 3 hours, during which the liquid is frequently stirred—or after standing, if more convenient, over-night—the greater part of the liquid is decanted off through a close filter, leaving about 40 c.c. of it in the beaker with the precipitate. The filter is washed with dilute hydrochloric acid, the washings being used to redissolve the precipitate in the beaker. After complete re-solution, the contents of the beaker are rendered ammoniacal by slowly dropping in dilute ammonia with vigorous stirring until the precipitate assumes as before a dense crystalline form. Excess of ammonia solution (sp gr. 0·880), equal to about one-fifth or one-sixth of the bulk of the liquid, is added and the whole allowed to stand with occasional vigorous stirring for at least one hour. The precipitate is then filtered, washed well with ammonia (sp.gr. 0·970), dried, ignited, and weighed as $Mg_2P_2O_7$.

The re-solution and second precipitation of the ammonium magnesium phosphate is an essential feature of the process, since in the first precipitation small quantities of magnesium oxalate are usually formed. The non-observance of this precaution has been a frequent source of 'high' results.

The presence of ammonium citrate and ammonium oxalate results in the retention in solution of a minute quantity of P_2O_5. In earlier days it was usual to precipitate the ammonium magnesium phosphate, in a flocculent form, by the sudden addition of ammonia and magnesium mixture, and under these circumstances (*see*, for example, the original directions of Fresenius) a very substantial correction was necessary for solubility of the precipitate. Crystalline precipitation, however, reduces this to a minimum, and the accurate determination by molybdic acid of the phosphoric acid in the evaporated and ignited filtrates obtained in a large number of analyses of numerous grades and varieties of phosphate indicates that, if the process be carried out as here described, the quantity of P_2O_5 which escapes precipitation corresponds to an average of approximately 0·0025 gram of $Mg_2P_2O_7$, which quantity must be added to the weight of $Mg_2P_2O_7$ obtained, together with half the weight of the small ammonia precipitate (obtained from the calcium oxalate precipitate), unless this was redissolved into the main filtrate (*see* above).

If the precautions herein set forth are observed, the results will be identical with those obtainable by the accurate working of the molybdic process as defined by Jörgensen or by Ullmann.

DIRECT MAGNESIUM PRECIPITATION WITHOUT REMOVAL OF CALCIUM.

This process consists in adding to the acid solution of the phosphate a large excess of citric acid, sufficient to prevent calcium precipitation, and of ammonia, and in the direct precipitation of the phosphoric acid by magnesium mixture, without re-solution. This process (with certain precautions) answers well for basic slag (*see* later), and in some hands appears to give good results with mineral phosphates. It does not, however, answer equally well for all phosphates, and the result, even when accurate, owes its success to a balance of positive and negative errors, since the precipitate finally weighed does not consist of pure $Mg_2P_2O_7$, as is assumed to be the case. For rough work, as in phosphate prospecting, when an error of 0·5 p.c. or so is of no moment, it is excellent, being expeditious and involving a minimum of trouble. It is essential that silica should be eliminated by preliminary evaporation of the acid solution to dryness as in the preceding section.

DETERMINATION OF FERRIC OXIDE AND ALUMINA IN MINERAL PHOSPHATES.

The solvent used should be hydrochloric acid rather than *aqua regia*. The latter is sometimes recommended. For many phosphates it is perhaps immaterial which solvent is used. But some phosphates (such as American river pebble phosphates) contain much pyrites. If *aqua regia* is used, this is dissolved and included as ferric oxide which is misleading, seeing that pyrites is not attacked by the sulphuric acid used in superphosphate making, and is consequently non-injurious. It should, therefore, be eliminated with the silica, as is the case if hydrochloric acid be used as the solvent.

There are two methods in use which accurately determine ferric oxide and alumina.

ACETATE METHOD.

Two grams of phosphate are treated with strong hydrochloric acid. The solution is evaporated to dryness and the residue redissolved in acid and water and filtered from the silicious residue. The filtrate is oxidised by addition of bromine water until orange coloured, nearly neutralised with ammonia, cooled and precipitated with a good excess of ammonium acetate solution containing an excess of acetic acid. After standing some hours, the precipitate is filtered off and washed with hot water.

The bulky precipitate contains all the ferric oxide and alumina (as phosphates), together with a varying quantity of calcium phosphate. It is dried, ignited, and weighed. It is then dissolved in a very small quantity of hydrochloric acid and about 1 gram of citric acid and 0·5 gram of ammonium oxalate added, slight excess of ammonia, and then excess of acetic acid. After simmering gently for half an hour the calcium oxalate is filtered off, ignited, and weighed as carbonate. The phosphoric acid is then determined, exactly as in the citric-oxalic-magnesium method of phosphate analysis already described—except that the operation is conducted all through in solutions of very small bulk. The sum of the lime and phosphoric acid deducted from the weight of the ammonium acetate precipitate will give the ferric oxide and alumina. The iron is determined by precipitating the total filtrates and washings from the precipitation and reprecipitation of the ammonium magnesium phosphate with ammonium sulphide. If allowed to stand for an hour or two at a temperature of about 80°C., the precipitate settles well, and may be rapidly filtered, washed with hot water to which a little ammonia and ammonium sulphide are added, ignited strongly and weighed as Fe_2O_3. The alumina is obtained by difference. The method is tedious, but accurate.

MODIFIED GLASER METHOD.

The following method, modified from that of Glaser (which originally, but incorrectly, assumed a constancy of composition of the precipitate of mixed phosphates) is somewhat shorter, and gives results identical with those obtained by the method just described.

Four grams of the phosphate are treated with about 25 c.c. of strong hydrochloric acid and evaporated to dryness. The residue is taken up with 10 c.c. of strong sulphuric acid, about an equal bulk of water being cautiously added. After digestion in a water-bath for about ¼ hour, the cake of calcium sulphate is well broken up by stirring with a glass rod, and the whole contents of the beaker are washed into a 200 c.c. flask with ordinary strong alcohol (methylated spirit), and allowed to remain for an hour with frequent shaking. The contents are then made up (with spirit) to 200 c.c., again well shaken and filtered rapidly. Of the clear filtrate, 100 c.c. (=2 grams of the sample) are evaporated in a glass or porcelain basin until the residue fumes and begins to 'char,' when it is washed with a little hot water into a beaker and mixed with sufficient bromine water to make it strongly orange-coloured. After standing for half an hour, the liquid is heated nearly to boiling and precipitated with slight excess of ammonia, kept in a water-bath for half an hour, and made slightly acid with acetic acid. The precipitate (which, under these conditions, contains only phosphoric acid, ferric oxide, and alumina) is filtered off, washed with a slightly ammoniacal 20 p.c. solution of ammonium nitrate, dried, ignited, and weighed. It is then dissolved in a little hydrochloric acid, 1 gram of citric acid is added to the solution, which is then made ammoniacal, and the phosphoric acid determined by precipitation with magnesium mixture. The total bulk of fluid should be kept within about 100 c.c. In this case, the precipitate of ammonium magnesium phosphate does not need re-solution and re-precipitation, seeing that no oxalate is present. The iron is precipitated from the filtrate with ammonium sulphide, as in the preceding process, and the alumina is arrived at by difference.

Lasne Process for Direct Determination of Alumina.

Objection has been sometimes raised to the fact that, while in the processes already described, ferric oxide is determined directly, alumina, on the other hand, is taken by difference. The following process, as described by H. Lasne, affords a correct method for the direct determination of alumina. It has been frequently tested by the writer of this article, in whose experience it gives results substantially identical with those obtained by the two differential methods already quoted. In either case, whether a direct or an indirect method be used, success depends upon delicacy of manipulation and strict attention to the details prescribed.

Five grams of phosphate are treated with hydrochloric acid, the solution being evaporated to dryness, taken up with 60 c.c. of 10 p.c. hydrochloric acid, and digested at about 100°C. for 1 hour. The solution is diluted to 500 c.c., and filtered, 125 c.c. being taken for the determination of alumina. Five grams of caustic soda (free from silica and alumina) and 1 gram of sodium phosphate are dissolved in 20 c.c. of distilled water in a nickel basin. Into this solution the 125 c.c. of phosphate solution are poured, with constant stirring, and kept for about an hour at a temperature of about 100°C., with occasional stirring, preferably with a nickel spatula. The liquid is cooled, and made up to 250 c.c. in a glass flask. The contents are filtered, and 200 c.c. of the filtrate (=1 gram of the phosphate sample) mixed with 30 c.c. of a solution of ammonium chloride (125 grams per litre), sufficient hydrochloric acid being added to dissolve such precipitate as is formed. Ammonia is then added in very slight excess. After boiling for 5 minutes, the precipitate is filtered off, washed slightly once with water, and redissolved through the filter into the original beaker with a little 10 p.c. hydrochloric acid, the filter being washed with water five or six times. The solution is treated with 3½ c.c. of a solution of pure ammonium phosphate (10 grams per 100 c.c.), and ammonia added till a permanent precipitate is formed, and then sufficient dilute hydrochloric acid to again dissolve the precipitate. The fluid is diluted to 250 c.c., when 10 c.c. of a solution of ammonium hyposulphite (15 grams per 100 c.c.) are poured in. After half an hour's boiling, five drops of a saturated solution of sodium acetate are added, and, after 5 minutes' further boiling, the precipitate is filtered off and washed seven or eight times with water. The precipitate, which is granular and not gelatinous, is ignited to constancy, and assumed to have the composition of pure aluminium phosphate. Its weight multiplied by 0·418 gives the alumina in 1 gram of the sample.

Analysis of Superphosphate, Dissolved Bones, &c.

'Moisture' is conventionally determined by simply drying to constancy at 100°C. The result should, in such cases, be stated as 'moisture' (*i.e.* loss at 100°C.), because the figure obtained is not moisture in the true sense, since it includes a varying quantity of water of hydration. True moisture can only be determined by drying to constancy *in vacuó* over sulphuric acid. The result in that case should be stated as 'true moisture' (*i.e.* loss *in vacuó*).

Determination of Soluble Phosphate.

Formerly in England, and still in America, solubility was determined by fractional exhaustion with successive small quantities of cold water (with or without a final exhaustion with hot water). On the continent of Europe it has long been usual to dissolve in a large bulk of water at one operation. The former method usually extracted somewhat more phosphoric acid than the latter, since some interaction occurs on dilution between the dissolved phosphoric acid and the 'insoluble' phosphate. As this depends upon the chemical composition of the original phosphate, and also on the degree of dilution, the differences in the results obtained by the two methods of extraction are variable—being sometimes negligible, but occasionally serious.

The following method of extraction of soluble phosphate, adopted at a meeting of the International Congress of Applied Chemistry, is now usually adopted in England, and is the method officially laid down in 1908 by the

Board of Agriculture for use under the Fertilisers and Feeding Stuffs Act :—

> 'In the case of superphosphates, dissolved bones and similar substances, 20 grams of the sample shall be continuously agitated for 30 minutes in a litre flask with 800 c.c. of water. The flask shall then be filled to the mark, and again shaken, and the contents shall be filtered.'

The mode of determination of phosphate in the water solution thus obtained is officially prescribed as follows :—

> '50 c.c. of the filtrate shall be boiled with 20 c.c. of concentrated nitric acid, and the phosphoric acid shall be determined by the molybdate method prescribed below.'

Official Molybdate Method (Board of Agriculture, 1908).

'To the solution, which should preferably contain from 0·1 to 0·2 gram of phosphoric oxide (P_2O_5), 100 to 150 c.c. of molybdic acid solution prepared as described below, or an excess of such solution, *i.e.* more than is sufficient to precipitate all the phosphoric oxide present in the solution, shall be added, and the vessel containing the solution shall be placed in a water-bath maintained at 70° for 15 minutes, or until the solution has reached 70°. It shall then be taken out of the bath and allowed to cool, and the solution shall be filtered, the phospho-molybdate precipitate being washed several times by decantation, and finally on the paper with 1 p.c. nitric acid solution. The filtrate and washings shall be mixed with more molybdic acid solution and allowed to stand for some time in a warm place in order to ascertain that the whole of the phosphoric oxide has been precipitated.

'The phospho-molybdate precipitate shall be dissolved in cold 2 p.c. ammonia solution, prepared as described below, and about 100 c.c. of the ammonia solution shall be used for the solution and washings. 15 to 20 c.c. of magnesia mixture prepared as described below, or an excess of such mixture, *i.e.* more than sufficient to precipitate all the phosphoric oxide present, shall then be added drop by drop, with constant stirring. After standing at least 2 hours with occasional stirring, the precipitate shall be filtered off, washed with 2 p.c. ammonia solution, dried, and finally weighed as magnesium pyrophosphate. The filtrate and washings shall be tested by the addition of more magnesia mixture.

'(*e*) *Preparation of molybdic acid solution.*

'The molybdic acid solution shall be prepared as follows :—

'125 grams of molybdic acid and 100 c.c. of water shall be placed in a litre flask, and the molybdic acid shall be dissolved by the addition, while the flask is shaken, of 300 c.c. of 8 p.c. ammonia solution, prepared as described below. 400 grams of ammonium nitrate shall be added, the solution shall be made up to the mark with water, and the whole added to 1 litre of nitric acid (sp.gr. 1·19). The solution shall be maintained at about 35° for 24 hours and then filtered.

'(*f*) *Preparation of magnesia mixture.*

'The magnesia mixture shall be prepared as follows :—

'110 grams of crystallised magnesium chloride and 140 grams of ammonium chloride shall be dissolved in 1300 c.c. of water. This solution shall be mixed with 700 c.c. of 8 p.c. ammonia solution, and the whole shall be allowed to stand for not less than three days and shall be then filtered.

'(*g*) *Preparation of the ammonia solutions.*

'The 8 p.c. ammonia solution shall be prepared as follows :—

'One volume of ammonia solution of sp.gr. 0·880 shall be mixed with three volumes of water. This solution shall then be adjusted by the addition thereto of more strong ammonia solution or water as required until the sp.gr. of the solution is 0·967.

'The 2 p.c. ammonia solution shall be prepared as follows :—

'One volume of 8 p.c. ammonia solution shall be mixed with three volumes of water.'

The soluble phosphate may be determined equally well by applying to 100 c.c. of the water extract, obtained by the official method of extraction (=2 grams of the original superphosphate) the oxalic-citric-magnesium process as described for raw mineral phosphates, omitting the evaporation to dryness; but in disputed cases in which litigation may arise, the molybdate method should be used.

Both 'soluble phosphate' and 'insoluble phosphate' in England are always stated in terms of tricalcium phosphate. On the Continent, it is usual to state them in terms of P_2O_5, with or without a statement of the equivalent $Ca_3P_2O_8$. The 'insoluble' phosphate is estimated by determining the 'total' phosphate and deducting from it the soluble phosphate.

Determination of Total Phosphate in Fertilisers.

This may, in most cases, be carried out by the methods already described for the analysis of raw mineral phosphates, materials containing much organic matter being first incinerated.

The official method prescribed in England under the Fertilisers and Feeding Stuffs Act, however, which should be adhered to in disputed cases, is the molybdate method, already described under soluble phosphate.

The official prescription of the Board of Agriculture for determination of total phosphate in fertilisers is as follows :—

> 'A weighed portion of the sample, in which portion, if necessary, the organic matter has been destroyed by ignition and the silica removed by appropriate means, shall be dissolved in nitric acid and boiled, the solution being made up to a definite bulk. The phosphoric acid shall be determined in an aliquot part of the solution by the molybdate method prescribed' (*see* above).

Reverted Phosphate.

The 'reverted' phosphate in superphosphate may be determined as follows: 2 grams of the sample are stirred up in a beaker with successive quantities of 50 c.c. of water, each portion, after settling, being decanted off through a filter. The water-soluble phosphate having been thus approximately removed, the matter on the filter is washed back into the beaker with a little water, and the undissolved matter is treated with either neutral or ammoniacal ammonium citrate solution. In America, neutral citrate is used, made by dissolving 185 grams of citric acid, neutralising with ammonia (using alcoholic solution of coralline as indicator), and making up to 1 litre. In France, a strongly ammoniacal solution is used, made by dissolving 400 grams in 1 litre of ammonia of sp.gr. 0 920.

In the American method, the water-insoluble residue referred to is digested with 100 c.c of (neutral) citrate solution for half an hour with frequent shaking. In the French method, it is digested with 100 c.c. of (ammoniacal) solution for 12 hours, agitating occasionally during the first hour.

The matter undissolved by the citrate solution is filtered off, washed, ignited, and dissolved in hydrochloric or nitric acid and the phosphoric acid determined in it. The difference between water-soluble phosphate and total phosphate gives the insoluble (including reverted) phosphate. The difference between this and the phosphate undissolved by citrate solution is taken as 'reverted' phosphate.

Analysis of Basic Slag.

In the analysis of basic slag, it is now usual to determine (*a*) the percentage of 'fine meal,' (*b*) the percentage of total phosphoric acid, and (*c*) the percentage of phosphoric acid soluble in a 2 p.c. solution of citric acid.

Fine meal.—This is determined by sifting a given weight of the sample through a sieve made of brass gauze, having approximately 10,000 apertures per square inch, of the make known as 'Amandus Kahl, No. 100 E, Hamburg,' and weighing the residue.

As the size of the apertures depends upon the gauge of the wire, the use of any other make or pattern of gauge is a possible source of discrepancy. In well-ground slag from 80 to 90 p.c. should pass through the sieve. This is called the percentage of 'Fine meal.'

The *total phosphoric acid* may be determined as in mineral phosphates or as in other fertilisers.

An excellent method for slag, however, giving (by an admitted balance of errors) results identical with those of the molybdic process, is as follows: Treat 2 grams of the slag with strong hydrochloric acid and evaporate to dryness. Take up with 15 c.c. of hydrochloric acid and 25 c.c. of water, adding 20 grams of powdered citric acid. The silica is filtered off and washed, and the filtrate and washings (measuring about 170 c.c.) are cooled, a large excess of magnesium mixture is added and about 50 c.c. of strong ammonia. The liquid is stirred continuously for 15 or 20 minutes by aid of a mechanical stirrer, and allowed to stand with occasional stirring for 2 hours. The precipitate is filtered off, dried, ignited, and weighed as $Mg_2P_2O_7$.

N.B.—This process is largely in use on the Continent, without observance of the initial precaution of evaporating the acid solution to dryness to remove soluble silica. If the slag be merely digested with acid and the liquid filtered and precipitated without having been evaporated to dryness, the results may be seriously in excess of the truth. This has been pointed out by several investigators, but is not yet well recognised.

The phosphate soluble in 2 p.c. solution of citric acid is determined, according to the method prescribed in the official directions of the Board of Agriculture:—

'*Phosphate soluble in 2 p.c. citric acid solution.*

'5 grams of the sample shall be transferred to a stoppered bottle of about 1 litre capacity. 10 grams of pure crystallised citric acid shall be dissolved in water, the volume shall be made up to 500 c.c., and the solution shall be added to the weighed portion of the sample in the bottle. To lessen the possibility of caking, the portion of the sample in the bottle may be moistened with 5 c.c. of alcohol or methylated spirit before the citric acid solution is added; and in that case the volume of the citric acid solution shall be 495 c.c. instead of 500 c.c. The bottle shall be at once fitted into a mechanical shaking apparatus, and shall be continuously agitated during 30 minutes. The solution shall then be filtered through a large "folded" filter, the whole of the liquid being poured on the paper at once. If not clear, the filtrate shall be again poured through the same paper.

'50 c.c. of the filtrate shall be taken and the phosphoric acid shall be determined by the molybdate method prescribed.'

It may be added that 100 c.c. of the solution (=1 gram of sample) can be used equally well for the molybdate determination.

The phosphate in the citric acid solution of the slag is frequently estimated by direct precipitation with magnesium mixture after adding a large excess of ammonium citrate. The results, however, are inaccurate (being too high) unless the citric acid solution of the slag is first evaporated to dryness with hydrochloric acid to eliminate soluble silica. If this precaution be taken, the results compare well with those of the molybdate process—which, on the whole, is quicker, and therefore preferable.

Analysis of Potash Salts.

Some commercial potash salts are of complex constitution, others are approximately simple salts. The methods of determining such constituents as calcium, magnesium, chlorine, &c., do not differ from those ordinarily employed in inorganic analysis, but the essential determination, namely, that of potash, may be described. Broadly speaking, two methods are in use, namely, the perchloric acid method and the platinum chloride method. The perchloric acid method was formerly but little used in this country, but owing to the great increase in the cost of platinum-chloride has now come into wide use, and ranks with the platinum chloride method as "official" in England.

The following are the details of the method for determining potash in potash salts and in fertilizers officially prescribed in England in 1918 for use under the Fertilisers and Feeding Stuffs Act:—

'Determination of Potash.

'(*a*) *Muriate of potash free from sulphates.*

'A weighed portion of the sample (about 5 grams in the case of concentrated muriate of potash or 10 grams in the case of low-grade muriate) shall be dissolved in water, the solution shall be filtered if necessary and made up to 500 c.c. The potash shall be determined in 50 c.c. of the solution either by the platinum chloride method, or by the perchloric acid method, prescribed below in clauses (*e*) and (*f*) of this paragraph.

'(*b*) *Salts of potash containing sulphates.*

'A weighed portion of the sample (about 5 grams in the case of concentrated sulphate of potash or 10 grams in the case of kainit or other low-grade salts) shall be boiled with 20 c.c. of hydrochloric acid and 300 c.c. of water in a half-litre flask. Barium chloride solution shall be cautiously added, drop by drop, to the boiling solution until the sulphuric acid is completely precipitated. Any slight excess of barium shall be removed by the addition of the least possible excess of dilute sulphuric acid. The liquid (without filtration) shall be cooled and made up to 500 c.c. and filtered. 50 c.c. of the filtrate shall be taken and evaporated to dryness, and shall then be moistened with concentrated hydrochloric acid, again evaporated to dryness, treated with a little dilute hydrochloric acid and filtered if necessary. The potash shall be determined in the filtrate either by the platinum chloride method, or by the perchloric acid method, prescribed below in clauses (*e*) and (*f*) of this paragraph. If the solution contains phosphates, iron, manganese, or other substances that would interfere with the determination of potash, the method prescribed in clause (*c*) of this paragraph is to be used instead of the method prescribed in clause (*b*).'

(In calculating the results, international atomic weights are used, including Seubert's atomic weight for platinum, which, in the international table for 1911, is given as 195·2.)

'(*c*) *Potash in flue-dust.*

'Ten grams of the sample shall be gently ignited in order to char organic matter, if present, and shall then be boiled with 300 c.c. of water. 10 c.c. of concentrated hydrochloric acid shall be added slowly so as not to check the boiling, which is to be continued for a further 10 minutes after the addition of the last portions of acid. The liquid shall be filtered into a half-litre flask and raised to the boiling-point; and to the boiling liquid powdered barium hydroxide is to be added until there is slight excess. The liquid shall then be cooled, made up to 500 c.c., and filtered. Of the filtrate, 250 c.c. shall be treated with ammonia solution and excess of ammonium carbonate, and, while boiling, with a little powdered ammonium oxalate. It shall then be cooled, made up to 500 c.c. and filtered. Of the filtrate, 50 c.c. or 100 c.c., according to the amount of potash expected, shall be evaporated in a porcelain dish to dryness. If desired, nitric acid may be added during the evaporation after free ammonia has been driven off. The residue is to be heated gently over a low flame until all ammonium salts are expelled, the temperature being carefully kept below that of low redness. The residue shall be moistened with concentrated hydrochloric acid, evaporated to dryness, treated with dilute hydrochloric acid, filtered, and the potash determined in the filtrate either by the platinum chloride method or by the perchloric acid method, prescribed below in clauses (*e*) and (*f*) of this paragraph.

'(*d*) *Potash in guanos and mixed fertilisers.*

'Ten grams of the sample shall be gently ignited in order to char organic matter, if present, and shall then be heated for 10 minutes with 10 c.c. of concentrated hydrochloric acid, and finally boiled with 300 c.c. of water. The liquid shall be filtered into a half litre flask, raised to the boiling-point, and a slight excess of powdered barium hydrate shall be added. The contents of the flask shall be cooled, made up to 500 c.c. and filtered. Of the filtrate, 250 c.c. shall be treated with ammonia solution and excess of ammonium carbonate, and then, while boiling, with a little powdered ammonium oxalate, cooled, made up to 500 c.c., and filtered. Of the filtrate, 100 c.c. are to be evaporated in a porcelain dish to dryness. If desired, nitric acid may be added during the evaporation after free ammonia has been driven off. The residue is to be heated gently over a low flame, till salts are expelled, the temperature being carefully kept below that of low redness. The residue shall be moistened with concentrated hydrochloric acid, evaporated to dryness, treated with dilute hydrochloric acid, and filtered. The potash shall be determined in the filtrate either by the platinum chloride method, or by the perchloric acid method, prescribed below in clauses (*e*) and (*f*) of this paragraph.

'(*e*) *Platinum chloride method.*

'To the solution obtained as above described in clauses (*a*), (*b*), (*c*), or (*d*) of this paragraph a few drops of hydrochloric acid shall be added, if none is present, and also 10 c.c. or 20 c.c. (according to whether the portion weighed was 5 grams or 10 grams) of a solution of platinum chloride containing 10 grams of platinum per 100 c.c. After evaporation to a syrupy consistency on a water-bath, the contents of the basin shall be allowed to cool and shall then be treated with alcohol of sp. gr. 0·864, being washed by decantation until the alcohol is colourless. The washings shall be passed through a weighed or counterpoised filter paper, on which the precipitate shall be finally collected, washed with alcohol as above, dried at 100°, and weighed.

'The precipitate is to be regarded as K_2PtCl_6, and is to be calculated to its equivalent as K_2O.

'(*f*) *Perchloric acid method.*

'To the solution obtained as above described in clauses (*a*), (*b*), (*c*), or (*d*) of this paragraph and placed in a small glass or porcelain basin, 7 c.c., or 12 c.c. (according to whether the portion weighed was 5 grams or 10 grams), of a 20 p.c. solution of perchloric acid (sp.gr. 1·125) shall be added. The basin shall be placed on a hot plate or sand-bath and the contents evaporated until white fumes are copiously evolved. The precipitate shall be re-dissolved in hot water, a few drops of perchloric acid solution added, and the whole concentrated again to the fuming stage. After cooling, the residue in the basin shall be thoroughly stirred with 20 c.c. of alcohol of specific gravity 0·816 to 0·812 (95 to 96 p.c. of alcohol by volume). The precipitate shall be allowed to settle, and the clear liquid shall be poured through a weighed or counterpoised filter paper, or through a gooch crucible, draining the precipitate as completely as possible from the liquid before adding the washing solution. The precipitate shall be washed by decantation with alcohol (as above) saturated with potassium perchlorate at the temperature at which it is used, pouring the washings through the paper or gooch crucible on which the whole of the precipitate is finally collected, dried at 100°C., and weighed.

'The precipitate is to be regarded as $KClO_4$, and is to be calculated to its equivalent as K_2O.'

DETERMINATION OF NITROGEN IN FERTILISERS.

Nitrogen was formerly determined by the soda-lime combustion process which was modified by Ruffle (Chem. Soc. Trans. 1881, 87), so as to be also applicable to mixtures containing nitrates by means of introducing into the soda lime an admixture of sodium thiosulphate. The soda-lime process has now, however, been almost universally superseded by Kjeldahl's moist sulphuric acid combustion process, modified and improved by the successive labours of many investigators. In its present form it is one of the most accurate and reliable processes at the disposal of the analyst. It cannot be more clearly or concisely described than by quoting the directions laid down for its use in connection with the Fertilisers and Feeding Stuffs Act in the official regulations of the Board of Agriculture (1908):—

'The presence or absence of nitrates must first be ascertained.

'*Nitrogen in absence of nitrates.*

'A weighed portion of the sample shall be transferred to a Kjeldahl digestion flask; 10 grams of potassium sulphate and 25 c.c. of concentrated sulphuric acid shall be added, and the flask shall be heated until a clear liquid, colourless, or of light straw colour, is obtained. The operation may be accelerated by the addition of a small crystal of copper sulphate or a globule of mercury to the liquid in the digestion flask.

'The quantity of ammonia shall be determined by distillation into standard acid after liberation with alkali, and, where mercury has been used, with the addition also of sodium or potassium sulphide solution.

'*Nitrogen in mixed fertilisers when nitrates are present.*

'A weighed portion of the sample shall be transferred to a Kjeldahl digestion flask; 30 c.c. of concentrated sulphuric acid, containing 1 gram of salicylic acid, shall be added, and the flask shall be shaken so as to mix its contents without delay. The shaking shall be continued at intervals during 10 minutes, the flask being kept cool, and then 5 grams of sodium thiosulphate and 10 grams of potassium sulphate shall be added. The flask shall be heated until the contents are colourless or nearly so. Copper sulphate or mercury may be used as above described.

'The quantity of ammonia shall be determined as above prescribed.'

The quantity of material operated upon will vary according to its nature. In the case of materials rich in nitrogen, from 1 gram to 1·5 grams may be operated upon. On the other hand, in the case of materials composed chiefly of inorganic matter, and containing only small quantities of nitrogen—like low quality dissolved bone compounds—as much as 5 or 6 grams may be conveniently operated upon. It is usually convenient to make two simultaneous experiments on different quantities of the material, such as 1 gram and 1·5 grams, or 1·5 grams and 2 grams. The larger the quantity of material that can be satisfactorily dealt with, the less, obviously, is the multiplication of experimental error. Duplicate results, in careful hands, should differ by no more than a few units in the second place of decimals, when expressed as percentage of nitrogen in the material under examination.

It is pointed out in the regulations that all the materials used in either of the methods described must be examined as to their freedom from nitrogen, by means of a control experiment carried out under similar conditions with the same quantities of the reagents which are employed in the actual analysis, 1 gram of pure sugar being substituted for the weighed portion of the sample. The quantity of standard acid neutralised in the control experiment—which should be small if the materials are good—must be deducted from the total quantity of acid found to have been neutralised in the distillation of the sample. The observance of this precaution is of vital importance, seeing that small quantities of nitrogen compounds are frequently found even in sulphuric acid sold as pure for analysis; while traces of nitrates or nitrites may be present in sodium hydroxide.

In the above described modification of the Kjeldahl process for mixtures containing nitrates—due originally to Jodlbauer—phenol may be used, if desired, in place of salicylic acid, and 1 gram of zinc-dust may be used in place of the 5 grams of sodium thiosulphate. Zinc-dust, like the other materials, may contain traces of nitrogen, and must be carefully examined by being included with the other materials in a 'blank' experiment.

In the case of ammonium sulphate or other material containing nitrogen in the form of ammonium salts only (other than ammonium nitrate), the nitrogen may be determined by simple distillation with alkali.

Determination of nitrogen in sodium nitrate or in saltpetre. This may be carried out by several methods. One of the most convenient is the Ulsch method, which in the regulations of the Board of Agriculture is described as follows:—

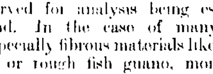
> 'One gram of the sample shall be placed in a half-litre Erlenmeyer flask with 50 c.c. of water. 10 grams of reduced iron and 20 c.c. of sulphuric acid of 1·35 sp.gr. shall be added. The flask shall be closed with a rubber stopper provided with a thistle tube, the head of which shall be half filled with glass beads. The liquid shall be boiled for 5 minutes, and the flask shall then be removed from the flame, any liquid that may have accumulated among the beads being rinsed back with water into the flask. The solution shall be boiled for 3 minutes more, and the beads again washed

with a little water. The quantity of ammonia shall then be determined as above prescribed. (*See Nitrogen in absence of nitrates.*)

'In cases in which the proportion of nitrates is small, a larger quantity of the sample shall be taken.'

General observations as to preparing samples for analysis. In the case of all samples, whether of fertilisers or of raw materials for use in their manufacture, it is obviously important to obtain a thoroughly representative portion for analysis. To this end it is usual, in the case of powdered fertilisers in dry or moderately dry condition, to pass the sample through a sieve, the perforations of which are about 1 mm. in diameter, pulverising the portions at first retained on the sieve—either in a mortar or, better, in a suitable mill—until they pass through. Adventitious materials which cannot be conveniently crushed, such as fragments of metal sometimes found in basic slag, must be removed and weighed, and subsequently allowed for in calculating the results of the analysis. Some materials, like shoddy, wool waste, or hair, cannot be powdered, but as a rule they can be passed through a shredding machine; or, if this is not possible, they must be finely cut up by hand. Some moist fertilisers do not admit of being passed through a sieve, and in dealing with these the analyst must use his discretion as to the best mode of obtaining an average sample. Crystalline or saline materials, like ammonium sulphate, potassium chloride, kainit, or sodium nitrate, are best prepared by mixing and rapidly grinding in a stoneware mortar, the portion reserved for analysis being especially finely ground. In the case of many moist materials, especially fibrous materials like shoddy wool waste, or rough fish guano, moisture is inevitably lost during the preparation of the sample. It is therefore necessary to separately determine the moisture in a large average portion of the original material before proceeding to pulverise the remainder. The moisture must also be determined in the fine material as prepared for analysis, and the results of the analysis recalculated so as to represent the percentages present in the sample in its original moist condition. In the case of raw mineral phosphates, it is usual to determine the moisture in a rough sample separately taken for this purpose, and to conduct the rest of the analysis on a separately prepared fine portion, after drying the latter at 100°—the results being returned on the dry basis, with a simple statement at the foot of the analysis of the percentage of moisture in the rough sample. But in the case of almost all other materials, the results of the analysis are returned as percentages of the material in its original moist condition. B. D.

FERULIC ACID. *m. Methoxy-p-hydroxycinnamic acid*



$$C_6H_3\begin{cases}CH{:}CH{\cdot}CO_2H & (1)\\ OCH_3 & (3)\\ OH & (4)\end{cases}$$

Occurs in asafœtida resin (Hlasiwetz and Barth, Annalen, 138, 64); in opopanax (Tschirch and Knilt, Arch. Pharm. 1899, 256), and in the resin of the black fir (Bamberger, Monatsh. 12, 441). The alcoholic extract of asafœtida resin is precipitated with lead acetate, and the precipitate, consisting of lead ferulate, is decomposed with sulphuric acid. It has been prepared artificially by means of Perkin's reaction by heating together vanillin, acetic anhydride, and dry sodium acetate, and decomposing the acetylferulic acid thus formed with potash (Tiemann and Nagai, Ber. 1878, 647); also by treating the methyl ether of *p*-amino-*m*-coumaric acid with sodium nitrite and decomposing the diazo-compound thus produced with water (Ulrich, J. 1885, 2093; *cf.* D. R. P. 32914; Frdl. i. 588). Rhombic needles, melting at 168°–169°, almost insoluble in cold water, readily soluble in alcohol, less soluble in ether (Tiemann and Nagai, Ber. 1876, 416). The solution gives with lead acetate a yellow flocculent precipitate, with ferric chloride a yellowish brown precipitate, reduces silver nitrate and Barreswil's (Fehling's) solution on warming. Fusion with caustic potash converts it into acetic and protocatechuic acids. Sodium amalgam reduces it to hydroferulic acid $C_{10}H_{12}O_4$.

FETTBOL *v.* Bole.

FIBRIN *v.* Blood and Proteins.

FIBRINOGEN *v.* Blood and Proteins.

FIBROLYSIN. Trade name for a combination of thiosinamine and sodium salicylate.

FICHTELITE. A hydrocarbon $C_{18}H_{32}$, found as white or yellowish platy crystals and crystalline crusts in the crevices of lignified pine wood in peat-bogs. The monoclinic crystals, both natural crystals and those obtained by recrystallising the material from alcohol or benzene, are interesting on account of their hemimorphic development, there being, as in crystals of cane-sugar and tartaric acid, no plane of symmetry. Sp.gr. 1·01; m.p. 46°; b.p. 355·2°; specific rotation in solution in chloroform $[\alpha]_D^{20^\circ} = +18{\cdot}08^\circ$. Analysis gives: C 86·79, H 13·02 p.c.; the vapour density is 8·6; and the molecular weight, determined by the cryoscopic method in benzene, 254·2. It has a high degree of stability, and can be distilled over red hot lead oxide without decomposition; derivatives are consequently difficult to obtain. Oxidation with chromic acid in an acetic acid solution yields two acids, the silver salts of which are $C_{15}H_{20}O_6Ag_2$ and $C_3H_5O_3Ag$. On distillation under 270 mm. pressure the bulk goes over at 290°–295° as a nearly colourless, viscous liquid with a splendid blue-violet fluorescence; this is dehydrofichtelite $C_{18}H_{30}$. Localities where fichtelite has been found are Redwitz and several other places in the Fichtel Mountains in northern Bavaria, Kolbermoor near Rosenheim in southern Bavaria, Borkovic and other places in Bohemia, Handforth in Cheshire, Shielding in Ross-shire, &c. For a review of the literature, *see* A. Schmidt, Centralbl. Min. 1901, 519; F. Plzák and V. Rosický, Zeitsch. Kryst. Min. 1908, xliv. 332; A. Rosati, *ibid.* 1912, l. 126. L. J. S.

FICOCERYLIC ACID $C_{12}H_{25}COOH$, m.p. 57°, is obtained from the wax of the wild fig-tree.

FIG. *Ficus carica* (Linn.). Many varieties are known, varying greatly in size of fruit—from 6 or 7 grams to 80 grams each—the average weight of the fresh ripe fruit being about 35 grams.

According to Colby (Reports of the Agric. Exp. Stat. California, 1892–1894), the average of 41 analyses of different varieties is—

Water	Sugar	Protein	Ash
78·9	15·6	1·4	0·6

The juice, amounting on the average to about 76 p.c. of the whole, contained 20·7 p.c. of sugar and 0·12 p.c. of free acid expressed as sulphur trioxide.

Balland (Rev. intern. falsif. 1900, 13, 92) found more water, less nitrogenous matter, and in addition about 0·28 p.c. fat, and 1·5 p.c. crude fibre.

Colby found the ash to have the following composition (mean of 3 analyses):—

K_2O	Na_2O	MgO	CaO	Mn_3O_4	Al_2O_3 & Fe_2O_3	P_2O_5	SO_3	SiO_2	Cl
55·8	2·4	5·6	11·2	0·2	2·2	12·8	3·9	4·3	2·0

Figs are eaten in the fresh, ripe state in districts where they are grown, but, for export, they are largely dried. The following is the average composition of dried figs (König):—

Water	Protein	Sugar	Free acid (as Malic acid)	Fat	Other carbohydrates	Fibre	Ash
28·8	3·6	51·4	0·7	1·3	5·3	6 2	2·7

The seeds of dried figs, according to Balland (*l.c.*), contain—

Water	Protein	Fat	Carbohydrates	Fibre	Ash
7·7	12·0	24·6	23·4	29·8	2·5

Hotter (Zeitsch. Nahrungsm.-Unters. Hygiene u. Waarenk. 1895, 9, 1) found, in dried figs from Smyrna, 0·0015 p.c. of boric acid. Wittmann (Zeitsch. landw. Versuchs Oesterreich, 1901, 4, 131) found 0·83 p.c. pentosans in fresh, 3·8 p.c. in dried figs.

According to analyses by Paladino (Biochem. Zeitsch. 1910, 24, 263), the following represents the composition of green and dried figs:—

	Water	Protein	Fat	Sugar	Cellulose	Mucilage, etc.	Ash
Green figs, pulp	80·0	0·7	0·3	16·2	1·3	0·8	0 7
,, ,, skin	86·0	(?)	0·1	5·4	5·8	2·7	(?)
Dried figs . .	57·0	4·1	2·2	26·0	8·0	0·2	2·5

It thus appears that the proportion of water in dried figs varies greatly.

When figs are moistened with warm water containing tartaric acid, they speedily ferment and yield a wine. This is largely made in Algeria, and is used for adulterating grape wine. When fig wine is evaporated to a syrup and allowed to cool, it solidifies, after 24 hours, to a crystalline mass consisting chiefly of mannitol, but containing glycerol and small quantities of sugar and organic acids. Mannitol is present in fig wine to the extent of 6 or 8 grams per litre, whilst in grape wine its amount does not exceed a few decigrams per litre. This fact may be used to detect fig wine as an adulterant of grape wine (Cables, Compt. rend. 1891, 122, 811).

The stems and branches of plants of the genus *Ficus* yield a viscid, milky juice containing caoutchouc or resinous substances resembling caoutchouc. *F. elastica* (Roxb.) is the species from which the largest proportion of this substance is obtainable. H. I.

FIG WAX *v.* WAXES.

FILBERT. The seed of *Corylus Avellana* (Linn.). The kernels have the following average composition (König):—

Water	Protein	Fat	Soluble Carbohydrates	Crude fibre	Ash
7·1	17·4	62·6	7·2	3·2	2·5

These were evidently in the dried condition; as usually eaten for dessert filberts contain much more water. The essential oil of the leaves was examined by Haensel (Chem. Zentr. 1909, i. 1476), who found it present to the extent of 0·04 p.c. It is light brown in colour, solidifies at about 30°, contains 18 p.c. of palmitic acid, and a paraffin hydrocarbon melting at 49°. It had an acid value 60·4, ester value 24·6, and its sp.gr. (in the super-cooled liquid condition) was 0·8844 at 25°. H. I.

FILICIC ACID *v.* FILIX MAS.

FILITANNIC ACID *v.* FILIX MAS and TANNINS.

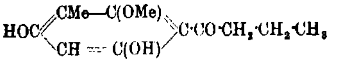
FILIX MAS (B.P.), Aspidium (U.S.P.). Male fern; *Rhizoma filicis.* (*Racine de fougère mâle*, Fr.; *Farnwurzel*, Ger.) The rhizome of male fern, *Aspidium filix mas* (Swartz), has been a favourite anthelmintic medicine since the times of Theophrastus, Dioscorides, Pliny, and Galen. (For botanical characters, *v.* Woodville (Med. Bot. 271), Moore and Lindley (Ferns of Great Britain, 14–17), and Bentl. A. Trim. 300.)

The early chemical investigations of the rhizome (see Pereira, Mat. Med. 3rd ed. 2, 959, and Poulsson, Arch. exp. Path. Pharm., 1891, 29, 1) show that, besides the constituents common to plants, it contains a peculiar *green fixed oil*, *tannin*, and a crystalline compound, first analysed by Luck (J. 1851, 558) and named by him *filicic acid.* These constituents are all found in the ethereal extract or 'oil of male fern,' in which form alone the drug is made use of in medicine.

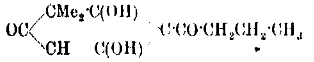
The green fixed oil is composed, according to Katz (Arch. Pharm. 236, 655) of the glycerides of oleic, palmitic, and cerotic acids, the chief constituent being triolein. The tannin, *filitannic* or *filicitannic acid*, is, according to Malin (Annalen, 143, 276), a glucoside; Wollenweber (Arch. Pharm. 1906, 244, 466) gives it the formula $C_{41}H_{44}O_{24}N,2H_2O$ (?). Its aqueous solution froths.

Filicic acid $C_{35}H_{42}O_{13}$ or $C_{35}H_{40}O_{13}$ is an amorphous colourless powder, melting at about 125°, and physiologically active. In boiling ethereal solution it is converted to its lactone *filicin* $C_{35}H_{40}O_{12}$ (Poulsson, *l.c.*), or $C_{35}H_{38}O_{12}$ (Boehm). This anhydride is inert and forms small yellow, rhombic leaflets, m.p. 184·5°. It is insoluble in water, hardly soluble in cold alcohol, readily in hot. By careful treatment with alkali it can be retransformed to the active acid (Poulsson). An insight into the constitution of filicic acid has been obtained by Boehm, who has isolated a number of other crystalline substances from fern extracts, and has made by far the most important contributions to our knowledge of the subject (Arch. exp. Path. Pharm. 1897, 38, 35; Annalen, 1898, 301, 171; 1899, 307, 249; 1901, 318, 230, 245, 253; 1903, 329, 269, 310, 338). All the substances isolated by Boehm appear to be either methylated phloroglucinylpropyl ketones, or to consist of two or three such ketone nuclei joined together by one or two methylene groups.

Aspidinol $C_{12}H_{16}O_4$, bright yellow crystals, m.p. 156°–161°, is the simplest of these substances. On boiling with zinc-dust and sodium hydroxide it is decomposed to methylphloroglucinolmonomethyl ether and *n*-butyric acid. It probably has the constitution—



Filicin (filicic acid), on the other hand, is the most complex, and consists of three such ketone nuclei, joined by two other carbon atoms. On boiling for a short time with zinc-dust and sodium hydroxide it yields, amongst other products, 'filicinic acid butanone,' m.p. 95°–97°, which is isomeric with aspidinol, and has the constitution—

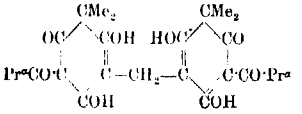


or one tautomeric with it.

By more prolonged boiling it breaks up into *n*-butyric acid and *gem*-dimethylphloroglucinol (filicinic acid). The latter substance gives, on oxidation, dimethylmalonic acid.

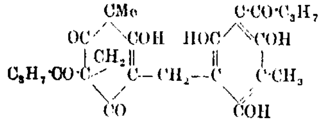
The other substances isolated by Boehm are composed of two ketone nuclei joined by one methylene group.

Albaspidin $C_{25}H_{32}O_8$, needles, m.p. 148°, consists of two filicinic acid butanone residues, and can be synthesised from this ketone by means of formaldehyde, whence the constitution :

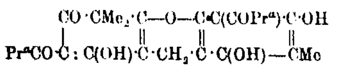


Phloraspin $C_{23}H_{28}O_8$, colourless needles, m.p. 211°, is similarly built up of methylphloroglucinol-*n*-butanone, and the methyl ether of phloroglucinol-*n*-butanone, two isomeric ketones $C_{11}H_{14}O_4$, lower homologues of those already referred to.

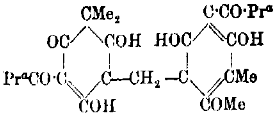
Flavaspidic acid $C_{24}H_{28}O_8$ exists in two modifications, melting at 92° and 156°, and appears to have on one side a four-membered ring—



By boiling hydriodic acid it is reduced to a xanthene derivative—



With the exception of filicic acid, all the above substances occur also in the rhizome of ***Aspidium spinulosum*** (Swartz), in which the filicic acid is replaced by *aspidin* $C_{25}H_{32}O_8$, m.p. 124·5° (=polystichin, Poulsson, Arch. exp. Path. Pharm. 1898, 41, 246). As the latter fern is often confused with *A. filix mas*, the commercial extracts of male fern may contain aspidin as well. The substance may be recognised in the crude extract by crystallisation (Hausmann, Arch. Pharm. 1899, 237, 544; Hausmann and Boehm, Annalen, 1903, 329, 321). Aspidin has most probably the constitution—



being built up of aspidinol and filicinic acid butanone. On reduction with hydriodic acid the same xanthene derivative is formed as is obtained from flavaspidic acid.

Most of the above substances are physiologically active on tape worms and other lower animals (Boehm; Straub, Arch. exp. Path. Pharm. 1902, 48, 1); the simplest one having any degree of activity is filicinic acid butanone; lower degradation products are inactive. It is difficult to attribute the anthelmintic action to any one substance in particular, but, according to Kraft (Arch. Pharm. 1904, 242, 489), this action is primarily due to yet another substance, *filmarone*, more complex than any isolated by Boehm. Kraft states that good extracts of male fern contain 3·5 p.c. filicic acid, 2·5 p.c. flavaspidic acid, 0·05 p.c. albaspidin, 0·1 p.c. aspidinol, 0·1 p.c. flavaspidin (probably identical with phloraspin of Boehm), and 5 p.c. filmarone. The last substance, $C_{47}H_{54}O_{16}$, is an amorphous brownish-yellow acid, melting at about 60°, and consisting of four different phloroglucinyl ketones. Boiling with zinc-dust and sodium hydroxide decomposes it into filicic acid, aspidinol, and various other substances. Whether filmarone is a chemical individual is not clear, but it seems to have met with a certain measure of clinical success.

For cases of poisoning by fern extracts, *see* Poulsson (Arch. exp. Path. Pharm. 1891, 29, 1): for detection of filicic acid in such cases, *see* Bocchi (Chem. Zentr. 1896, ii. 1137). G. B.

FILMARONE *v.* FILIX MAS.

FILROLYSIN. A mixed solution of allylthiourea (thiosinamine) and sodium salicylate. Used in the treatment of lupus and in softening scar-tissue.

FILTER-PAPER. The high-grade filter-paper used by the chemist for analytical work is usually made from cellulose obtained from flax or cotton, mostly in the form of waste material as yarn fabric or rags. Cotton cellulose is preferred owing to its low hydrating power, as compared with linen cellulose, under the action of 'beating,' resulting in what is termed a 'free' pulp, imparting 'bulk' or softness to the paper on which its efficiency as a filtering medium largely depends.

The filter-paper used in analysis, or for chemical work in general, should be as free as possible from inorganic matter. Lime and other inorganic impurities may be introduced into the pulp by the water used, or by the chemical operations in the paper-mill, such as bleaching. Iron and copper may be present from want of care in sorting the material employed. Silica and alumina may be owing to the presence of kaolin in the rags. The organic impurities consist mainly of starch, oil, and resinous matter—the last due to the natural presence of resin in the cotton fibre. The starch arises principally from the dressing in the rag material, and is largely removed by the treatment with boiling alkali and subsequent washing to which the rags are subjected. The small amount left in the pulp has the effect of 'sizing,' and thereby impairs the absorbing power and filtering speed of the paper. The amount of oil left in good filter-paper is usually not greater than 0·07 or 0·08 p.c. (Bevan and Bacon, Analyst, 1916, 159).

According to McBride and Scherrer (J. Amer. Chem. Soc. 1917, 39, 928), filter-paper frequently contains reducing substances which are extracted by the solutions passed through the paper, and which cause the filtrate to decolorise dilute permanganate solution, such as $\frac{N}{50}$ or $\frac{N}{100}$, especially when the titration is made on the heated liquid, whereby a relatively considerable error may be caused. The experiments indicated that the main bulk of the reducing matter is extracted by the first portion of the reagent passed through, and that if the filter be washed with 25 c.c. of the reagent before use, filtration and titration may be carried out, even on the heated liquid, without sensible error.

FILTER PUMPS. The filter pump is generally some form of dynamic air pump. Sprengel, in 1865 (Chem. Soc. Trans. 18, 9), showed how a very perfect vacuum could be obtained by the fall of mercury or other liquids, and Bunsen, in 1868 (Annalen, 148, 277), showed how the difference of pressure so obtained could be utilised in greatly improving the ordinary process of filtration.

This application has given a name to all these instruments, though they are applicable to nearly all the purposes for which any ordinary air pump or aspirator might be used. Many of them, with a continuous supply of falling liquid or of steam or other gas, under pressure, are almost automatic in their working, and far more convenient than any piston air pump.

The pumps used in laboratories are of three kinds:

1. Barometer or weight pumps.
2. Momentum or pulsation pumps.
3. Injection or pressure pumps.

1. Barometer pumps. Of these there are two varieties, the statical or Geissler pump, and the dynamic or Sprengel pump.

The Geissler pump was invented about 1855 by Geissler, and in it air is exhausted by the alternate emptying and filling with mercury of a vessel forming the upper part of a barometric column. It is simply an application of the Torricellian vacuum. Geissler used this pump in the production of his vacuum tubes, and since his time it has been modified and improved by many inventors; Töpler (Dingl. poly. J. 1862, 423), also Poggendorf, Mitscherlich, Pflüger, Joule, and others.

The Sprengel pump, in its simplest form, is a plain tube of small but uniform bore, and of a length rather greater than that of the barometric column of the liquid used in it. It is furnished with a side tube near its upper extremity. The continuous falling of the liquid, generally mercury or water, produces the exhaustive effect, which is slow at first, but can be made to give a more perfect vacuum than is possible by any other means. The improvements of the Sprengel pump have been chiefly towards quickening its action, and have been described by McLeod, Swan and Stearn, Gimingham, Weinhold, and others. Crookes' experiments on the radiometer and radiant matter were rendered possible by the use of the Sprengel pump, and in the manufacture of incandescent electric-lighting lamps these barometric pumps have had a considerable industrial application. The Sprengel pump, worked by water, was that used by Bunsen in his improved mode of filtration, and this application—the most important to the chemist—gave rise to the many inventions described below in this article.

2. The momentum or pulsation pump. This was described by Jagn, in 1872 (Pogg. Ann. 148, 317). It consists of a plain tube of moderate length, with side tube near the upper end. In action, the soft indiarubber tube connecting the apparatus with the water supply (of a very moderate fall or pressure) is ingeniously made to act as a valve by which the water is alternately admitted and shut off. We have thus an action similar to that of the hydraulic ram, in which the momentum of a column of liquid comes into play. In the ram, water is raised in front by the momentum; in this pump, air is pulled in behind. Modifications of the Jagn pump have been described by Thorpe (Phil. Mag. 1872, 249), also by Foote, Linnemann, and O. Witt. As these pumps are intermittent in their action, they work more slowly than others which are continuous, and have been superseded by them.

3. Injector or pressure pumps. These consist of tubes of various forms, but generally furnished with a jet or narrow neck in front of a wider neck or expanding mouthpiece. Any liquid or gas under pressure, such as water or steam, may be used to work them, and in any position.

They are similar in principle and construction to the water pump (Fig. 1) described by James Thomson (B. A. 1852–3) or the Giffard steam injector, patented in 1858. The principle of the injector was, however, partially known long before. Hawksbee, in 1719, found that on blowing through a tube into a small box, the air escaping by another tube opposite the first, the pressure in the box became less than that of the atmosphere; and D. Bernouilli, in 1738, found that water from a higher source flowing towards the wide end of a conical tube could lift water from a lower level through a side tube attached near the narrow part of the conical tube. Between 1830 and 1850, the steam-jet aspirator was used by Carson, G. Stephenson, and others. Clement and Desormes, in 1855 (Ann. Chim. Phys. 36, 69),

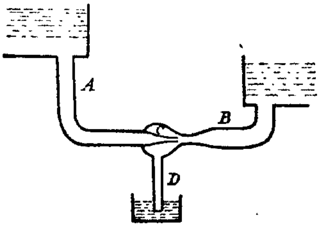


FIG. 1

showed that a light plate brought near a small orifice in the side of a reservoir of compressed air was attracted, and remained rapidly oscillating near the opening. This effect can be shown by blowing between the fingers against a piece of paper, or by blowing between two cards, as described in Weinhold's Physics, 312. All these experiments are examples of the passage of a fluid through an expanding mouthpiece, causing a diminished pressure as compared with that in front, which in each case is that of the atmosphere.

The first injector air pump for laboratory use was that of Christiansen, described in 1872 (Pogg. Ann. 196, 155). In Fig. 2, A is a piece of thick-walled indiarubber tubing, perforated at B by a hot wire, and constricted at C by a ring drawn over the tube. On inserting at B a short piece of bent glass tubing drawn out to a jet, and connecting the top end of A with the water supply under moderate pressure, air is drawn in through the bent tube, and a considerable vacuum obtained.

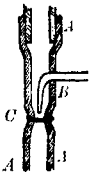


FIG. 2.

Other early forms of injectors were described by Lovett (Chem. News, May, 1874, 209) and Casamajor (*ibid.* June 27, 1875, 33); and soon after these dates numerous forms were invented for the use of chemists, dentists, &c.

The experiments of W. Froude (B. A. 1875), though made for a different purpose, afford an excellent explanation of the action of injectors.

Froude showed that water under any head H (Fig. 3), passing through a contracted pipe, does not exert an excess of pressure on the converging surface, which it meets, as is frequently stated, but that the pressure is least at the contracted part, as shown by the levels in the gauge glasses *a*, *b*, *c*, *d*, *e*. If the pipe be much contracted, the pressure can be still more reduced, so that if two cisterns, A and B (Fig. 4), be connected by such a contracted pipe, a portion of the pipe at C may be removed without the flow of the liquid being interfered with; the water rising in the cistern B only slightly below its level in A. At F, in the central line of the connecting pipe, the full head of pressure H is exerted, but there is practically no movement, while at C there is no pressure, but very rapid movement. The pressure and velocity of movement are therefore convertible and complementary, and the differences of pressure at any two points vary as the differences of the squares of the velocities at those points. In any given case the pressure observed, *plus* that which has been lost in producing velocity, is constant and equal to the total head of water H (Figs. 3, 4, 5). If we modify Froude's experiment and cut off the pipe at E (Figs. 4, 5), the pressure at E is simply the general pressure of the atmosphere, and all the pressure due to the head of water in A has been changed into velocity, but the velocity at C must be greater than the velocity at E by as many times as the sectional area of the pipe at C is contained in its area at E. The velocity at C being so much greater than at E, the pressure must be less, and therefore less than that of the atmosphere. The tube G (Fig. 5) may be regarded as a gauge to show the minus pressure, and if this gauge be supplied with mercury, the latter may rise to near the height of the barometer. In place of water or liquid under pressure, air, steam, or any gas under pressure may be used, and injector air pumps worked by steam have been proposed by Lovett, Kochinke, Teclu, and others.

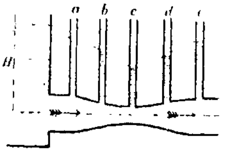


FIG. 3.

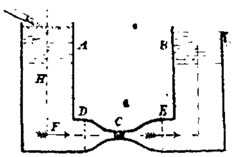


FIG. 4.

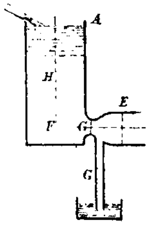


FIG. 5.

Injector air pumps, worked by water, may be classified:

(*a*) As in Figs. 6, 7, where the water enters by a jet placed over a constricted tube or neck, the air being drawn in on all sides round the jet of water. The ratio of the areas of the jet and neck in this form is generally 1 : 2, or their respective diameters 1 : 1·4.

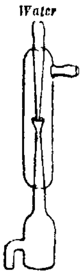


FIG. 6.

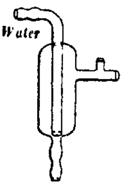


FIG. 7.

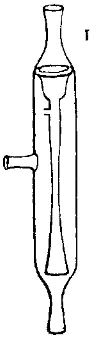


FIG. 8.

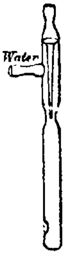


FIG. 9.

(*b*) As in Fig. 8, where the jet and neck are continuous and the air enters on one side only.

(*c*) As in Fig. 9, where the general form is similar to (*a*), but the air enters by a very narrow jet and the water filling the body of the pump enters all round the jet.

These differences in construction are of little importance in the practical working of the instruments, but by altering the width of the apertures, pumps suited to different pressures can be obtained. Pumps with very narrow apertures work best with small quantities of water at very high pressures, whereas pumps with wider apertures require much more water at a low pressure. As the water passing through these instruments is practically a falling body, on multiplying the weight of water in pounds used per minute by its head or pressure in feet, we obtain in foot-pounds the power required to produce the exhaust in one minute's working of the pump. Compared in this manner, the low-pressure pumps are less efficient than those working at higher pressures.

In using these injectors, care should be taken to have a sufficient and constant water supply. The water tap turned full on should supply in one minute twice to three times the quantity required by the pump in the same time. In towns and large buildings where many persons are using the water at different levels, the pressure is often very variable, and a reservoir of water under pressure is necessary. A simple form devised by the author is a strong iron bottle (or an iron boiler) capable of standing a greater pressure than is likely to be required, say up to or over 100 lbs. per square inch. This bottle A (Fig. 10) has one tube passing to the bottom connected by a T-piece with the water-supply pipe, and it may carry a pressure gauge if desired. The connection with the water tap may be made with lead pipe and soldered joints, or with sound rubber tubing encased in a double thickness of strong canvas sewn over it, the connections being well bound with copper wire. The bottle being air-tight and water-tight under pressure, and full of air when connected with the supply pipe, the air cannot escape, but is compressed by the pressure of the water. Thus at 15, 30, or 45 lbs. pressure the bottle becomes half, two-thirds, or three-fourths full of water, and with a variable pressure in the supply pipe keeps the pressure more constant, and maintains the supply for some time, depending on the size of the bottle or reservoir. Passing from this reservoir, the supply pipe is next led to the pump B, which may be conveniently fixed out of the way on a board against the wall behind the laboratory table. The board carries a barometric gauge to show the vacuum obtained.

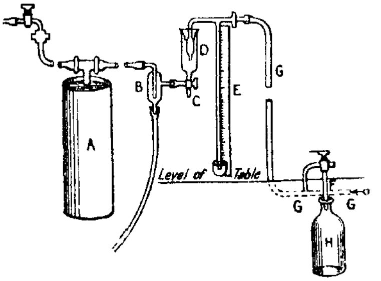


FIG. 10

Passing from the pump, the water used runs into the sink on the laboratory table, or if desired it may be connected with a box or drum provided with an overflow at a certain height, so as to give a blast of air under pressure suitable for general blowpipe work. The vacuum tube from the pump is connected by means of the tap C (Fig. 10) with the safety tube D, having a Bunsen valve fitted inside to the end of the vacuum tube, thence with the barometric gauge E and the laboratory vacuum tube G.

Fig. 11 shows in full size the tap C in Fig. 10, which is fitted to the bottom of the safety tube and to the laboratory vacuum tube at each working place on the tables F (Fig 10). An ordinary good gas tap, which should be specially ground so as to be as air-tight as possible, has the little screw and washer at the bottom of the plug removed and a hole bored from C into the ordinary through hole of the tap, the latter being soldered up at one side at D, so that the hole is from the bottom to one side only, and the plug is then trimmed and reground. A piece of tubing, FF, is then soldered on to the body of the tap and a pointer, E, soldered on to the top of the plug to point which way it is open. When the plug is turned across in the ordinary position of a closed tap, it is closed to both A and B; when the pointer points to A, it is open towards A, and if towards B to B. The tube FF is fitted air-tight by means of a stopper in the bottle H (Fig. 10).

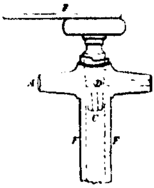


FIG. 11.

By means of these taps (devised by the author in 1883), one pump can do all the exhaustion work in an ordinary laboratory for a number of filtrations going on simultaneously. The pump is connected with a main pipe of soft lead tubing passing along or under the laboratory tables, and at each worker's place is a bottle like H (Fig. 10) fixed below the table, the tube FF from it rising above the table. One end of the tap, say A, is connected with the vacuum main pipe by soldered lead tubing; the other end of the tap is connected by a flexible tube with the filtering apparatus or other vessel to be exhausted.

In using this arrangement, all the vacuum supplied at B must come from the bottle below FF, and not from the main pipe, which is then shut off. When the vacuum is not required at B, the tap is turned towards A to raise the degree of exhaustion in the bottle. As these bottles are of half-gallon or 2·2 litres capacity, a moderate vacuum in one of them (say half to three-quarters the height of the barometer) is sufficient for a filtration on the small scale, and as there are a number of such bottles in the laboratory they form together a vacuum reservoir of some magnitude available at once without waiting. If well fitted, the taps retain the vacuum for several days. A lute made by dissolving indiarubber in vaseline at as low a temperature as possible is of good service for these taps and connections.

The author made a series of comparative tests of the pumps in common use (J. Soc. Chem. Ind. 1887, 64–76). With a supply and pressure of water suited to each pump, and exhausting receivers of the above capacity, 2·

TABLE OF THE FIRST MINUTE'S WORKING OF THE PUMPS.

Name of pump	(a) Exhausting the receiver of 2·2 litres capacity											(b) Blowing power			
	Water pressure in pounds per square inch										Ratio of volume of air pumped out to water used	Water pressure in lbs. per sq. inch	Litres per minute		Ratio of air to water
	5	10	15	20	25	30	35	40	45	50			Air blown	Water used	
	Vacuum obtained in one minute														
	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.					
Alvergniat Frères (glass) (Fig. 6)	—	302	395	442	481	515	564	577	—	—	Varies from 0·27 to 0·29	40	5·90	6·32	0·93
„ „ (brass)	—	182	240	322	385	426	452	468	—	—	„ 0·24 to 0·29	40	4·35	5·08	0·85
Arzberger and Zulkowsky (brass)[1]	221	286	374	468	530	—	—	—	—	—	„ 0·14 to 0·16	25	4·36	9·52	0·46
„ „ with outflow tube in lowest position	—	330	419	507	562	—	—	—	—	—	„ 0·14 to 0·16	20	4·51	10·8	0·42
„ „ in highest position	—	156	213	273	342	478	497	512	—	—	„ 0·17 to 0·28	40	3·90	5·44	0·79
Bendix (brass)	—	226	299	356	406	442	468	478	—	—	„ 0·22 to 0·25	40	4·65	5·92	0·79
Bulk (glass),[2] (Fig. 9)	—	160	226	286	338	395	426	458	—	—	„ 0·24 to 0·32	40	2·65	4·26	0·62
Finkener (glass)[3]	—	—	—	—	447	551	582	—	—	—	„ 0·21	35	6·38	8·24	0·77
Fischer (glass),[4] (Fig. 7)	—	203	247	286	322	380	408	419	—	—	„ 0·33 to 0·35	40	5·15	3·52	1·46
„ (brass, by Dreyer & Co.)	—	135	205	268	312	351	390	421	—	—	„ 0·35 to 0·54	40	3·24	2·26	1·48
„ (brass, by Desaga)	—	226	261	364	390	416	439	491	—	—	„ 0·36 to 0·37	40	4·73	3·80	1·22
„ (brass, copy by ?)	—	143	226	265	283	312	346	380	—	—	„ 0·30 to 0·40	40	2·90	2·75	1·05
Geissler (glass)[5]	—	117	162	179	205	234	252	307	329	—	„ 0·21 to 0·25	40	1·76	3·53	0·50
Knecht (brass)	—	—		161	252	278	286	296	299	—	„ 0·35 to 0·54	40	0·90	1·73	0·52
Körting (brass)[6]	195	333	426	499	546	582	—	—	—	—	„ 0·15 to 0·23	30	4·15	8·32	0·50
Mawson and Swan (No. 1 glass),[7] (Fig. 8)	—	182	239	273	320	331	439	458	—	—	„ 0·23 to 0·28	40	3·00	4·88	0·62
„ „ (No. 2 glass)[8]	—	138	179	202	247	289	432	447	—	—	„ 0·16 to 0·28	40	2·95	4·96	0·59
„ „ (No. 3 glass)[9]	—	130	192	229	266	309	335	376	—	—	„ 0·28 to 0·36	40	2·25	3·01	0·75
Muencke (No. 971 glass)	—	276	338	395	429	458	486	—	—	—	„ 0·18 to 0·19	35	3·30	8·52	0·39
„ (No. 970 glass)	234	307	398	473	515	—	—	—	—	—	„ 0·14 to 0·16	20	2·76	8·60	0·32
„ (No. 948 small brass)	—	—	—	—	—	356	390	413	432	458	„ 0·53 to 0·56	50	2·75	2·86	1·12
„ (No. 952 adjustable brass with three-way tap)[7]	—	—	—	356	426	486	507	535	—	—	„ 0·31 to 0·34	40	4·00	4·72	0·85

[1] Ann. d. Chem. u. Pharm. Bd. 1875, 176, p. 327. [2] Ber. d. deutsch. chem. Ges. 1876, p. 1871. [3] Winkler's Industrie Gaze, i. p. 23. [4] Dingl. poly. J. 1877, 221, p. 136 and 225, p. 342. [5] Sent out about 1876. [6] Sent out about 1880. [7] Sent out about 1876. [8] Sent out about 1877. [9] Sent out about 1879.

litres, vacua corresponding to from half to three-quarters of the height of the barometer could generally be obtained in one minute's workings; such vacua are quite sufficient for ordinary filtrations.

As the apparent size of these instruments is somewhat misleading, the quantity of water used is the real test of size; pumps of the same construction but of different sizes would exhaust a receiver at different rates, but in proportion to the water used.

The table on p. 198 gives the results in brief of tests made with the pumps most frequently found in use; first, in exhausting a receiver of 2·2 litres capacity, and second, in blowing air, with the exhaust tube of the pump open to the atmosphere. The results of the first minute's working only are given, though the tests were carried on to 10 minutes. In each case, those pumps which worked best during the first minute continued to so do throughout, and came nearest to the height of the barometer at the end of the exhaustion.

The blowing power of each pump is also a test of its exhaustive power, as in blowing with the pump open to the atmosphere it is practically exhausting an infinitely large receiver.

Of the high-pressure pumps, those of Fischer, Bulk, Knecht, and Muencke's brass pumps give good results, and of the low-pressure pumps, which use more water, those of Arzberger and Zulkowsky, Finkener, and Körting, are good. Alvergniat's glass and brass pumps are intermediate in character, and work well through a considerable range of pressure.

Given abundance of water at sufficient pressure, the pumps which give the most rapid exhaustions are those of Finkener, Körting, Alvergniat, Arzberger, and Zulkowsky; but where economy of water is desired, the high-pressure pumps ought, if possible, to be used. Though considered as machines doing work for the power put into them, none of these injectors is very perfect, yet they are exceedingly convenient, and it will be observed that all those tested give *at some particular* pressure in one minute's working sufficient vacua for filtrations and similar laboratory work.

In choosing an instrument for laboratory use, one should ascertain the average quantity of water per minute delivered by the fully open water tap and also the average pressure in the closed water pipes. The pump selected should require not more than half the quantity of water delivered by the open tap, and should work well at from half to two-thirds of the pressure in the closed pipes.

In recent years, there has been a great increase in the use of injectors for industrial purposes, including many chemical and mechanical applications.

Generally, the energy applied in injectors gives about 50 p.c. in real effective duty, but their low initial cost, absence of moving parts, and of metallic or corrodible surfaces, and above all the perfect control under which they can be applied and regulated, more than make up for the low percentage of duty. Thus they are ideal machines where ordinary pumps or exhausters are inadmissible, and are excellent as auxiliary agents to more complicated or permanent apparatus for improving the draught in furnaces, the ventilation in mines and workshops, and the conveyance or transfer of corrosive liquids and gases, and of mixtures of solids and liquids, such as ordinary sewage, and of mixtures of sand and water. The removal of ashes in steamships is most conveniently effected by this means.

Injectors are used to produce a blast for the division or spraying of liquids, as in the burning of liquid or semi-liquid fuels under boilers, the coating of large surfaces by spraying the paint over them, even where they are difficultly accessible. The spraying of water into the leaden chambers in the manufacture of sulphuric acid is found to be more efficient than the admission of steam.

Similarly, the exhaust obtained by injectors worked by air, steam, or water, is applied in the various methods of vacuum cleaning. These applications are well described in the book on The Transportation of Gases, Liquids, and Solids, written and published by Oskar Nagel, of New York, 1910.

A convenient circulating pump which may be constructed out of ordinary laboratory materials, and is adapted to maintain a flow of water around most complex apparatus at almost any desired rate, has been contrived by J. S. Morgan (Chem. Soc. Trans. 1915, 107, 1710). A simple valve to prevent water from being sucked back into the filtering flask has been described by Hutchinson (Chem. News, 1912, 106, 99). T. F.

FILTRATION is the operation of mechanically separating finely divided solids from their associated liquids by means of porous media.

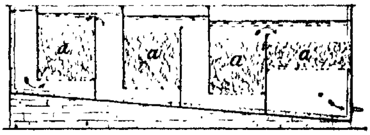


Fig. 1.

The media used may consist of loose material, such as sand; a compact body, such as biscuit pottery; or woven or felted materials, such as cloth, paper, and felt. It may be remarked, however, that the real filtering medium is often the layers of separated solids, the materials mentioned above only serving as convenient supports. A loose filtering medium is generally adopted where the proportion of liquid is relatively large and the solids of little value. The filter shown in Fig. 1 may be used for cleansing an effluent. Each compartment, *a*, is filled with wood-wool, kieselguhr, or similar material which is replaced when choked. Fig. 2 is a section of

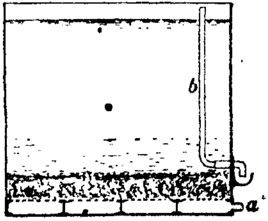


Fig. 2.

a filter in which the bed, 6–10 inches deep, is formed by means of layers of graded materials, as gravel, sand, coke, limestone, &c. The upper layer of (finest) material is retained in place by a covering of stout wire gauze or perforated metal, when the shovels of the workmen are removing the separated solids. By providing a movable basket with a bottom of gauze which may be lifted by means of a crane, an economy in handling is effected where labour is dear. This filter is intended for vacuum working by connecting the lower pipe opening *a* to a vacuum vessel and pump. The swinging pipe *b* enables the workman to remove rapidly the upper layers of liquid, which may become clear by subsidence. In filters of this type, where the solids are of no value, their removal is often accomplished by stirring the upper layers and running to waste the turbid liquor. The direction of the liquor current is often reversed for the same purpose. Water supplies are usually filtered through sand filters, and by the addition of a coagulant (to form large aggregations), such as aluminium sulphate, pressure may be used, and the rate of filtration increased from 4 to over 200 vertical inches per hour. The ordinary domestic water filter, in which hollow cylinders of biscuit pottery are used as the filtering medium, is occasionally met with in a large form in chemical factories. To obtain suitable porosity, such filtering devices are made of clay mixed with finely divided combustible materials such as wood, cork, &c., which are burnt off in the process of firing. Filter stones are made on this principle, in which the layers are of varying porosity. For very fine precipitates in acid solutions filters provided with such 'stones' or 'tiles' are most successful, and are far more economical than filter presses using woollen cloths. A common form is shown in Fig. 3, and consists of a lead-lined steel cylinder holding three (one or more) filtering trays, which may be attached to the front cover and moved in and out on rails. The 'tiles' are provided on the underside with grooves or with feet to rest on the floors of the trays, and are cemented in position. Outlet pipes with valves passing through temporary joints on the front or back of the cylinder provide for the discharge of the filtrate.

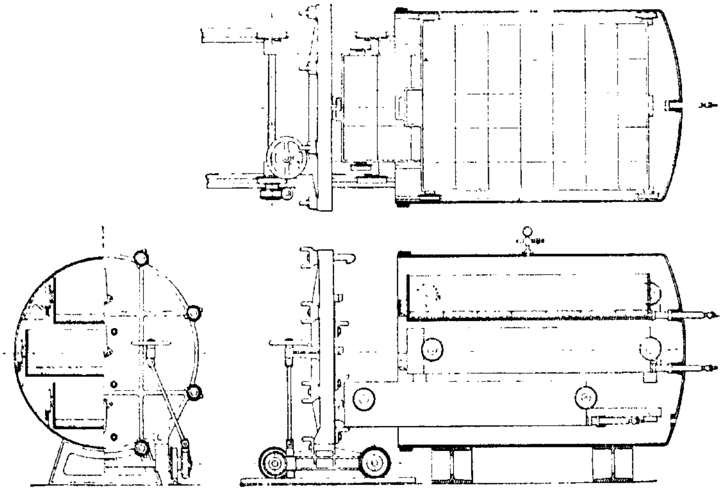


FIG. 3.

The trays may be filled with sludge or mother liquor while outside the cylinder, or simple arrangements may be made for the purpose after the admission of compressed air when filtration is proceeding. Sight glasses are sometimes provided for inspection, especially to ensure that washing commences before the cake of precipitate begins to crack. Generally, the operator waits until air appears at an outlet before the valve of that particular tray is closed. The cake is washed in a similar way, and since there is little diffusion, the amount of washing water required is very small. The rate of filtration through these 'tiles' does not alter after many months of use, and the filtrate is bright from the start.

The simplest filtering apparatus in which a woven fabric is used consists of a frame to which the fabric is secured. A wicker basket is sometimes used, and this arrangement is most convenient where the cake of material is to be folded in the cloth and squeezed in a press for the removal of more liquor. Washed graphite and similar materials are often separated in long and narrow canvas bags tied to spouts in the delivery channel from the washing apparatus. A simple form of vacuum filter, using a woven fabric or a disc of paper as a filtering medium, is shown in Fig. 4. It is made in stoneware, the perforated plate *b* supporting the fabric and the vacuum pump being connected with the nozzle *a*.

Filtration may be carried out in centrifugal machines which are conveniently driven from below. The rotating basket is provided with a removable cage carrying the filtering cloth, which is bodily removed and replaced at each operation. Another system by which rapid filtration may be obtained with a small area of filtering surface consists in mounting the filter cloth on a perforated drum, as shown in the diagrammatic section (Fig. 5). The drum revolves about once a minute in a bath of the liquid to be filtered which is maintained at a constant level. The filtrate is removed from the inside of the drum under a vacuum of 10 or 12 inches of mercury, produced by connecting the hollow spindle of the drum with a vacuum vessel and pump. The deposited solids on the surface of the drum are washed by the water jets *b* and finally removed by the scrapers *c*.

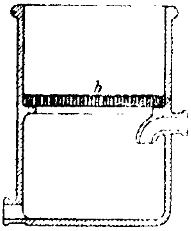


FIG. 4.

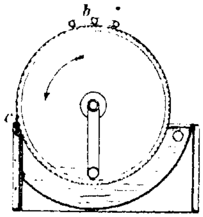
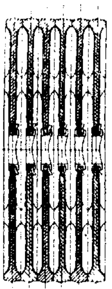


FIG. 5.



A type of filter which is now coming into common use is the vacuum leaf filter. In this filter a group of flat filtering bags, provided with means to prevent them from collapsing, are surrounded by the liquid to be filtered, and a partial vacuum applied to the interior of the bags or leaves. When cakes of most efficient thickness are formed, either the mother liquor or the group of filtering leaves is moved, and washing water applied. After washing, the cakes may be dislodged from the leaves by a puff of compressed air. It will be realised that, during the formation of the cake, deposition will take place fastest at those points where the resistance to the flow of liquor is least, i.e. the porosity of the cake is automatically maintained constant all over, with a result that the washing must also be uniform and efficient.

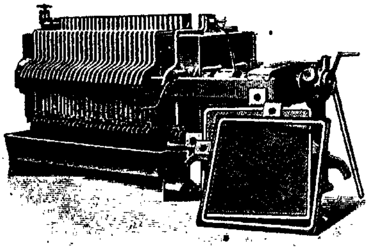


FIG. 6.

The most important apparatus for filtration is the filter press (Fig. 6)—a mechanical arrangement by which an enormous area of filtering surface may be provided in a very small space, with the additional advantage that the operation may be carried out under almost any conditions of pressure. A number of plates covered with filter cloth are put together in a frame to form a series of hollow spaces in which the liquor to be filtered is forced. The central area of each plate is provided with projections or ribs to support the filter cloth and to enable the liquid which has passed through the cloth to leave the press through a channel in the plate. The solid matter is retained in the hollow spaces, and is discharged in cakes by separating the plates. The hollow spaces between the plates are formed either by raised margins on the plates, *Recessed plate type* or *chamber press* (Fig. 7), or by means of distance frames, the width of which determines the thickness of cake formed, *Flush plate and distance frame type* or *frame press* (Fig. 8). The plates and frames are made of material suitable for the liquors to be treated, and may be of cast iron, gun-metal, aluminium, hard lead, wood, &c. Iron plates are sometimes covered with sheet tin, lead, zinc, or ebonite. Chamber presses are to be preferred where the solids do not form a solid cake, or where there is risk of choking the narrow channels leading to the frames of the frame press. The pressure used and the thickness of cake are also determined by the character of the separated solids. With slimy solids, a thin plate and a low pressure are desirable; the cake may be ½ inch thick and the pressure may be that produced by placing the feed tank a few feet above the press. Easily filtered solids may be separated in a frame 3 inches wide at a pressure of over 100 lbs. per square inch. Frames 1 inch wide are used in general work.

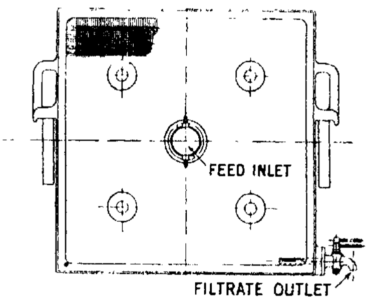


FIG. 7.

Owing to the facility of forming channels through the press from plate to plate by

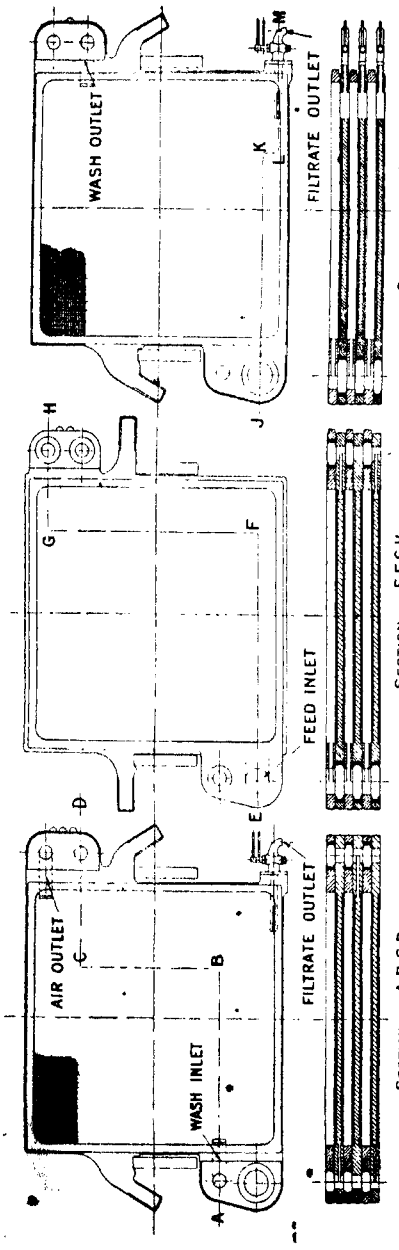


FIG. 8.

providing holes in each plate in similar positions, many complicated operations may be performed. The liquid treated may be continuously maintained at a suitable temperature by providing channels in each plate for the circulation of a hot or cold fluid. By the provision of rubber diaphragms and water under high pressure, the cakes may be squeezed before removal from the press. Washing the cakes is simply accomplished by feeding the washing water by means of a special channel behind the filtering cloths of alternate plates, and allowing it to leave the press by a channel connected to the remainder of the plates (Fig. 8). As the washing water rises in the cakes, the imprisoned air is allowed to escape by means of air cocks.

The joints between the plates at each of the holes which form a channel through the press, are made by rubber packing rings or by the arrangement of short pieces of rubber pipe so that the internal pressure of the liquid ensures tightness.

Air vessels of ample dimensions should be fitted to pumps feeding filter presses to prevent variations in pressure. Taps are usually provided on each plate for the delivery of the filtrate, so that any plate may be cut out should its effluent become turbid. In starting the filtration, the pressure is applied gradually to build up the filtering layer; with some substances, the filtrate is always turbid for a second or two. In presses where the plates deliver their filtrate into a common channel, small cylindrical filters supported in cages are sometimes provided to stop this action and also, by choking, to automatically stop the delivery of a turbid filtrate through the piercing of any filter cloth. Presses for volatile liquids are usually provided with a cover dipping into an oil or water seal, and connected on occasion with suitable recovery plant.

The materials used as filter cloths are simply well-made strong fabrics—cotton material for most purposes, woollen fabric for dilute acid liquors, and for certain fine work, silk. The filter paper used should be crinkled to admit of its expansion in contact with its supporting fabric. Wire gauze or perforated metal plates are used for some filtrations, a filter bed being first formed by running into the press a pulp of vegetable or mineral fibres.

The rate of filtration and washing is comparable with the flow of liquids through capillary tubes, provided that it is understood that the total area of the passages through the cake is affected by the pressure and by the viscosity of the filtrate or washing liquid.

If washing be carried out at pressures which do not break down the cake, the rate of washing will depend on the filtration pressure, and is directly proportional to the washing pressure, and inversely proportional to the thickness of the cake and the viscosity of the washing liquid. During filtration, however, owing to the pressure affecting the porosity of the cake, the rate is usually proportional to the pressure raised to a power less than unity. An increase in the viscosity of the liquid increases the value of this index. In the case of a coarsely granular or crystalline precipitate, the value of this index may be 0·6, but with fine amorphous material it may not be more than 0·2. With gelatinous precipitates the effect of pressure on the porosity of the cake is generally so serious, that only enough pressure to ensure the flow of the mother liquor may be used.

With precipitates requiring much washing, it is good practice to filter at a lower pressure than that at which washing is carried out, for not only is the rate of washing increased, but the efficiency of the washing is improved. It will be noticed that in the ordinary filter press the thickness of cake during washing is twice that during filtration, when the mother liquor is delivered in the middle of the cake.

J. W. H.

FINE BLUE, GENTIAN BLUE 6B, SPIRIT BLUE, OPAL BLUE, BLEU DE NUIT, BLEU LUMIÈRE. The hydrochloride, sulphate, or acetate of triphenylrosaniline and triphenylpararosaniline (*v.* TRIPHENYL-METHANE COLOURING MATTERS).

FIRE-CLAY. A refractory clay suitable for the manufacture of fire-bricks for furnace-linings, gas-retorts, crucibles, glass-house pots, &c. The qualities required for such goods are that they should retain their size and shape during firing, possess strength and durability, resist high and sudden changes of temperature, and the corrosive action of hot liquids and gases. The attainment of a combination of these qualities best suited to any particular purpose will depend more on the physical characters of the fire-clay than on its chemical composition, and actual trial of samples is desirable rather than detailed analyses. It is, however, essential that the material should consist mainly of aluminium silicate, with only small amounts of alkalis, calcium, iron (especially as pyrites), and titanium, all of which have the effect of lowering the fusibility. The presence of free silica also has the same effect, but to a much less degree. Pure kaolinite ($H_4Al_2Si_2O_8$, m.p. about 1820°) and quartz (m.p. 1760°, as tridymite) are both highly refractory, but mixtures have a lower melting-point than either, with a minimum of 1630° for 90 p.c. kaolin and 10 p.c. quartz. This is, however, still above the lower limit (about 1600°) usually allowed for a fire-clay. The best fire-clays occurring beneath beds of coal in the English coal-measures contain Al_2O_3, 20–30 p.c., and SiO_2, 50–70 p.c. (corresponding to about 3–23 p.c. of free silica). With increasing amount of silica these clays gradually pass into sandstones, which are also used as refractory materials; *e.g.* ganister (*q.v.*) and the so-called Dinas 'clay' from the Vale of Neath in Glamorganshire, containing as much as 98 p.c. of silica. The analyses at top of next column are of fire-clays from: I. Stourbridge in Worcestershire, by C. Tookey (also P_2O_5, 0·06 p.c.). II. Dowlais in Glamorganshire, by E. Riley. III. Better-bed fire-clay from Bowling in Yorkshire, by J. W. Westmorland (also TiO_2, 0·87 p.c.). IV. Plastic fire-clay from St. Louis, Missouri, quoted by H. Ries, 1908 (also SO_3, 0·35). (For a large series of analyses of British and foreign fire-clays, *v.* Percy's Metallurgy: Fuel, 1875, 87.)

	I.	II.	III.	IV.
SiO_2 . . .	65·10	67·12	68·12	57·62
Al_2O_3 . .	22·22	21·18	26·69	24·00
Fe_2O_3 . .	—	1·85	2·00	1·9
FeO . . .	1·92	—	—	1·2
CaO . . .	0·14	0·32	1·15	0·7
MgO . . .	0·18	0·84	0·59	0·3
K_2O . . .	0·18	2·02	1·17	0·5
Na_2O . . .	—	—	—	0·2
H_2O . . .	7·10	4·82	0·20	10·5
Moisture . .	2·18	1·39	—	2·7
Organic matter .	0·58	0·90	SO_3	0·35
	99·60	100·44	99·92	99·97

The celebrated fire-clay of Stourbridge in Worcestershire is remarkable for the small amount of contraction that it undergoes when fired, the shrinkage of the unrefined clay being in some cases as low as 1 p.c. For the purpose of reducing shrinkage, fire-clay is often mixed with 'grog,' *i.e.* burnt fire-clay, which has also the effect of giving sufficient porosity to the fire-bricks to enable them to withstand sudden changes of temperature. A greater degree of porosity, with correspondingly less strength, required in the fire-bricks of household stoves, is often produced by mixing sawdust with the clay.

A fire-clay occurring in the millstone-grit series at Glenboig in Lanarkshire, has been examined by J. W. Gregory and D. P. McDonald (Proc. Roy. Soc. Edinburgh, 1910, xxx. 348, 374), who find that the fine-grained clay substance forming the bulk of the material is present as minute rounded granules about 0·001 mm. in diameter; this is amorphous and not crystalline, and is referable to the mineral species halloysite rather than to kaolinite. Embedded in it are abundant grains of quartz, some grains of felspar, and minute crystals of a rhombohedral carbonate referred to sideroplesite (a variety of chalybite).

(*V.* H. Ries, Clays, their Occurrence, Properties, and Uses, 2nd ed. New York, 1908; A. B. Searle, An Introduction to British Clays, Shales, and Sands, London, 1912; A. B. Searle, Refractory Materials, London, 1917.)

L. J. S.

FIRE EXTINCTION AND PREVENTION. Combustion, as it exists in ordinary cases of fire, is due to the rapid combination of the burning material with the oxygen of the air at temperatures above the ignition-point, and it may be extinguished either by lowering the temperature of the burning mass below the point necessary for the continuance of the combustion, or by cutting off the access of air, and so depriving the combustion of the oxygen which is essential for its support.

The usual method adopted for extinguishing a fire is to pour on to the blazing material a large volume of water, and this acts partly by rendering heat latent in its evaporation, and so cooling down the burning mass, and partly by the steam generated driving back the air and so giving time for the cooling action to take effect.

The force with which the water is thrown upon the burning body also produces a considerable effect by sweeping the flame from the surface and so extinguishing the burning gaseous products.

Although, in round figures, 1 lb. of well-dried wood on combustion will convert about 5 lbs. of water into steam, yet in the early stages of a fire it is only the surface of the wood that is burning, so that the 5 lbs. of water will have a useful effect over a considerable surface, whilst the steam generated occupies a volume about 1700 times that of the water used.

In the use of water, a certain amount of discretion is necessary, as otherwise undesired results may follow. For instance, in a big warehouse fire, the lower portion soon becomes a mass of red-hot carbonaceous matter, and if water is recklessly played into this, the water is almost instantly turned into steam, which is decomposed in passing through the surrounding red-hot carbon, forming a mixture of hydrogen and carbon monoxide, known as 'water gas.' This gas is inflammable, and by its combustion adds to the general blaze, whilst, if it escapes being ignited, it may collect under ceilings and roofs, where, mixing with air, it forms a highly explosive mixture liable to be ignited by any chance flame or spark.

If, however, the water is directed on to the top of the mass, the carbonaceous matter is cooled downwards, so that the steam evolved does not pass through the glowing carbon, and there is thus the minimum generation of inflammable products.

A fire can also be extinguished by practically smothering it by cutting off the supply of air, and although this is rarely practicable, yet the closing of all doors and windows, by reducing the quantity of air available, checks the combustion.

Water is useless for the extinction of burning oils and spirits, as these, being lighter than water, float on the surface and continue to burn. The best way of treating a fire of this kind is to throw on it sawdust, sand, or earth or anything that will serve to keep the air away, and so cause the flame to die out.

Sawdust is more efficient than sand, as it floats on the burning liquid. For the extinction of small petrol fires, such as may occur in a garage, the British Fire Prevention Committee recommend the use of a mixture of sawdust, 1 bushel (about 12 lbs.), with 10 lbs. of sodium bicarbonate. The sawdust floats on the burning liquid, smothering the fire, and the action is materially assisted by the carbon dioxide given off by the bicarbonate. A mixture patented in the U.S. as 'Foamite' consists of acid sulphate of alumina and bicarbonate of soda, the latter being mixed with a licorice decoction. The two solutions are run simultaneously into a mixing tank, and thence flow to the fire. Another foaming mixture is produced from solutions of sodium hydroxide (caustic soda) and ordinary alum. The separate liquids are kept ready for use at many stores and garages.

Attempts have been made to employ certain gases which are unable to support combustion, and which can be obtained commercially at a fairly cheap rate, but the advantages of this method are very doubtful, as, unless the whole of the surrounding air can be replaced by an atmosphere of the extinguishing gas, little good results. With a fire well alight in an open space, there is always a strong up-current of hot air and the products of combustion, so that any gas poured on to the fire would be carried upwards out of the area where it would be effective. In certain cases, however, as in confined spaces, this method has its uses. For instance, when a chimney is on fire, the combustion can be stopped by throwing a handful of sulphur on the fire in the grate. The sulphur burns, forming sulphur dioxide, and this being drawn up the chimney cuts off the supply of air from the burning soot and so extinguishes the fire.

The fact that certain gases and salts will extinguish a fire under certain conditions, has led to a variety of apparatus being designed, which are known under the name of chemical extincteurs, and vary in size from the small hand grenade to the horse-drawn or motor-driven chemical fire engine. Amongst the substances that have been brought into requisition for this purpose are such gases as carbon dioxide, hydrochloric acid gas, and ammonia, none of which supports combustion, and salts, like common salt and borax, tungstates and phosphates of the alkali metals, which form a protective coating on the surface of the combustible material.

Extincteurs may be divided into two classes, those in which carbon dioxide is provided in a liquefied form in a suitable capsule which can be pierced, or the gas generated rapidly from a charge of some carbonate, such as chalk or sodium carbonate, and an acid in the presence of a large volume of water. The pressure created by the evolution of the carbon dioxide in the containing vessel causes the water to dissolve the gas, and at the same time the pressure drives the water holding the gas in solution through the small hose and nozzle on to the fire. The water, as soon as it is subjected to the ordinary atmospheric pressure and heat, gives up the carbon dioxide, which, together with the steam, drives the air away from the burning material, whilst the cooling effect of the water is aided in the extinction by the salts in solution coating the heated mass.

The substances generally employed for the rapid evolution of the carbon dioxide are sodium carbonate and hydrochloric or sulphuric acid. These chemicals must, of course, be kept separate in the extincteur until the moment when the apparatus is brought into action, and there are several devices for securing this end. In some cases, the acid is contained in a thin glass bottle, which is left unsealed, at the top of the apparatus, whilst the carbonate is dissolved in the water. On turning the containing vessel upside down, the acid runs out of the bottle and mingles with the carbonate solution, causing immediate evolution of the gas. In other forms, the acid is in a sealed bottle, which is broken either by the release of a leaden weight inside the extincteur or by a blow on a plunger from outside. In the large forms of extincteur, the acid is contained in a bottle covered by a lead capsule, which can be pierced when necessary by a lever from outside the apparatus.

According to a Memorandum of the British Fire Prevention Committee (Tests on Fire Extinguishers, No. 186), bicarbonate of soda is usually employed, and care must be taken that the normal carbonate is not substituted in appliances designed for the former. The sulphuric acid should be 1·84 sp.gr., and the quantity used should be considerably less than the theoretical amount, so that the discharged liquid shall not be acid. One lb. of bicarbonate requires theoretically 9·3 ozs. of pure sulphuric acid, but the maximum quantity should not exceed 6 ozs. (by weight); smaller quantities down to 3·5 ozs. (weight) being equally effective. 0·75 lb. of sodium bicarbonate is sufficient for 2 gallons of water. An air space of 15 p.c. should be allowed for expansion of the liquid. The quantity of liquid should not exceed 3 gallons; with this amount the total weight of the extincteur will approximate to 0·5 cwt. Less than 1 gallon of liquid is too small to be of practical value. Dangerous pressures may be set up through the rapid generation of gas, especially if some obstruction at the valve or discharge exists, and several fatal accidents have occurred. The Committee recommend that all extincteurs should stand a hydraulic pressure test of 350 lbs. per square inch for 5 minutes, and the same applies to rubber hose. For certain situations it may be necessary to provide against the liquid contents freezing. Such salts as common salt or calcium chloride are employed, and these may set up corrosion of the metal container, solders, &c.

The second class of extincteur contains solutions of chemicals which coat the combustible materials, and in addition some of them employ chemicals which give off extinctive gases when subjected to the heat of the fire.

One of the most effective of the many solutions that can be used for this purpose is a solution of a mixture of sodium sulphide and ammonium chloride in molecular proportions. When this is thrown upon a hot fire, sulphur dioxide and ammonia are set free and smother the combustion, whilst the remaining combustible gets coated with a glaze of common salt.

For small fires and in the earliest stages of a fire in an enclosed space, extincteurs have proved very useful, but in the open and with a strong conflagration they are perfectly useless. A fire can rapidly and easily be extinguished if it be attacked within a few minutes of its starting, but in the majority of cases the fire originates during the night or when the place is shut up, so that by the time the outbreak is noticed the fire has gained a firm hold. In order to cope with these cases, numerous automatic devices, such as sprinklers, have been brought forward.

The first form of automatic sprinkler was introduced by Major A. Stewart Harrison, who had the idea of fitting the various rooms to be protected with a system of water pipes furnished at the necessary places with nozzles closed by easily fusible metal plugs. Any serious rise in temperature melted the plugs and started the flow of water through the various jets. Automatic sprinklers have been widely employed, and many different forms of apparatus, based in general on the release of a valve by the melting of strips of fusible alloy, are in use. The alloy commonly employed has the composition: bismuth, 4 parts; lead, 2 parts; tin, 1 part; cadmium, 1 part. Its melting-point is 65°C. (150°F.). Such fusible alloys have also found application in the automatic release of fireproof doors, shutters, &c.

It is the earlier stages of an outbreak of fire that are the most important from the point of view of ease of extinction, and in order to draw attention as soon as possible to an outbreak of fire in a building, such as a closed warehouse, automatic fire alarms have been devised, which on an undue rise of temperature, complete an electric circuit and ring a bell at a fixed place some distance away, say, at a fire station. The first forms of automatic fire alarm consisted of thermostats, which were sensitive thermometers, into the bore of which were sealed platinum contacts: as the temperature at the seat of the fire rose, the mercury of the thermostat expanded and completed an electric connection, causing a fire alarm to ring. But these were not certain in action, owing to the surfaces of the mercury and platinum becoming dirty and failing to establish contact, so to obviate this trouble, liquids having a cleansing action were introduced above the surface of the mercury to prevent any amalgamation or oxidation and ensure contact.

Another form of thermostat consists of a closed U-tube containing mercury, above the surface of which in each limb a volatile liquid is confined, and one limb is also surrounded by an insulating sleeve. A sudden rise of temperature will cause the liquid to volatilise more rapidly in the exposed limb, and so drive the mercury downwards: this action opens a closed electric circuit and closes a secondary system, which transmits a signal to any required spot. A differential thermostat is also used in connection with a fixed temperature thermostat, which remains stationary until a definite temperature is attained, and then has a long range for a small increase in temperature. After the first warning call has been given, a further rise in temperature gives a fire call.

Some alarms depend for their action upon the unequal expansion of metals, whilst others rely on the difference in rate of expansion between relatively large and small masses of the same metal; but in all cases, the movement brought about by the sudden rise of temperature is made to complete an electric circuit, and thus give warning at some predetermined place.

Although timber, like all organic substances, is combustible and is burnt away when subjected to a high temperature, yet it can be treated in such a way as to render it fireproof, so that, instead of causing it to burn away, intense heat merely chars it. Various substances have been suggested for this purpose, but many of these so-called 'antipyrenes' have proved unsuitable owing to their injurious effect upon the wood or upon the paints and varnishes used upon it. Common salt was at one time regarded with much favour as a fireproofing material for wood, but its hygroscopic properties ultimately caused its use to be abandoned.

Any substance which is to be used for fireproofing wood must have no deleterious action on the wood or corrode the nails and screws inserted in it, and must also be a stable and non-volatile body, otherwise, although the chemical might do the required work for a short period, if evaporated it would leave the wood as inflammable as before. The compounds, which practical experience has shown to be of use in this direction are ammonium chloride, ammonium phosphate, ammonium sulphate, calcium chloride, magnesium chloride, zinc chloride, zinc sulphate, stannous chloride, alum, borax, boracic acid, and the tungstates.

On a practical scale, the timber is run on a trolley into a large chamber, which is sealed up and then exhausted of air as far as possible. In this way, all the air and moisture are extracted from the cells of the wood, and, after allowing the wood to remain in the vacuum for some time to complete the extraction, the solution of chemicals is run into the chamber, the whole of the contents being then placed under hydraulic pressure, the amount of which is carefully regulated according to the nature of the wood under treatment, as the pressure required by a dense wood would crush and destroy the cells of a lighter timber. A gauge glass on the chamber shows when the right proportion of liquid has been absorbed, when the wooc is removed, drained, and dried at a definite temperature. The temperature to which the wood is subjected for drying purposes has a great effect upon the quality of the final product: too high a temperature will cause the wood to be brittle, but if the correct temperature be employed, the wood dries with all its original qualities unimpaired, but with the added property of non-inflammability.

Wood treated in this way, with mixtures of ammonium phosphate and boracic acid, can be worked in just the same way as non-treated wood: it has no injurious effect upon the tools, and will take paints, varnishes, and other decorative material as well as before treatment, whilst nails and screws do not corrode in it.

When wood thus treated is subjected to the action of a flame, charring takes place, as the cellulose of the wood fibre is still left, and under the action of heat is carbonised, but directly the flame is removed the charred mass blackens, and no spreading of the fire takes place. This effect is due to the chemicals used (chiefly ammonium phosphate and boracic acid) being forced into the cells of the wood by the course of treatment adopted, and once there it is practically impossible to remove them. Under the influence of heat, the ammonium phosphate decomposes, giving off ammonia and phosphoric acid, the former of which drives any air out of the wood replacing it by a non-combustible gas, whilst the phosphoric acid together with the boracic acid coat the cell walls with a glaze, which prevents the access of oxygen from the air to carry on further combustion. V. B. L.

FISCHER'S SALT, *Potassium cobaltinitrite.*

FISETIN, FISETOL *v.* YOUNG FUSTIC.

FISH OILS *v.* OILS AND FATS.

FLAGSTONE. A stratified rock which may be split along the planes of bedding into smooth-faced slabs, suitable for use as paving stones. If the stone is too absorbent, or finely laminated, the surface is apt to flake off by the action of frost. As hardness and durability are essential in a flagstone, sandstones are superior to calcareous or argillaceous rocks. The flaggy sandstones are generally micaceous; and their fissility may be partly due to the presence of mica along definite planes. The best English flagstones are derived from the lower coal-measures, the millstone grit, and the Yoredale rocks. Most of the flags used for paving the streets of London are obtained from the Yorkshire coal-field. The Elland flagstone, which is extensively worked, is a fine-grained micaceous sandstone from the lower coal-measures, or ganister series, extending with persistence through the coal-fields of Yorkshire, Lancashire, and Derbyshire. In Scotland, the lower old red sandstone yields paving slabs of very large size, the best-known being the dark-grey flagstones of Caithness and the Arbroath pavement of Forfarshire. The celebrated Caithness flagstone is one of the most important economic products of the old red sandstone. It is used locally as a building stone, and for use as stone flooring and staircases it has been exported to all parts of the world. The extensive works for Liebig's meat-extract on the River Plate in South America are floored throughout with Caithness flags. The stone is finely laminated, tough and compact, and its cementing material is siliceous, argillaceous, calcareous, and bituminous. The last of these, derived from the vast number of fossil fishes, renders the stone impervious to moisture. Analysis of stone from the Castle Hill quarries at Thurso, Caithness-shire, gave: SiO_2, 69·45; $Al_2O_3+Fe_2O_2$, 10·50; K_2O+Na_2O, 2·20; $CaCO_3$, 10·65· organic matter, 5·79 p.c. Weight per cubic foot, 157 lbs. L. J. S.

FLAKE WHITE. A variety of white lead (*v.* LEAD). The term is also applied to basic bismuth nitrate.

FLAME.

Incandescence of gases. When solids and liquids are heated beyond a certain temperature by an external source of heat, they become luminous, and the intensity of the light emitted increases very rapidly as the temperature is further increased. There is no reason to suppose that gases would behave differently except in degree, for according to the kinetic molecular theory of matter, light should arise from molecular vibrations occasioned by molecular collisions. It is doubtful, however, whether a gas has ever been brought by artifice into what may be called a state of purely thermal glow. The high transparency of gases to light is correlative to a very low emissivity. Iodine vapour, which is an exceptional gas in its absorptive power, does indeed glow when heated in a glass tube even when the walls are considerably below a red heat, but there is reason to believe that this glow is connected with the dissociation and recombination of the atoms in the iodine molecule (*see* especially Evans, Astrophys. J. 32; I, 1910).

Attempts to heat colourless gases, such as nitrogen, to the glowing-point, have given negative results.

In almost every case, *a flame is glowing gas*, and in view of the facts just recited we must add the qualification that *the glow is the accompaniment of chemical change.* It would be possible to refine upon this definition. A 'flame' of pure hydrogen in dustless air is, according to Stas, invisible, the radiation of short-wave length being wholly in the ultra-violet. Again, the glow observed during the decomposition of acetylene in a hot tube may be due wholly to the particles of liberated carbon and in no degree to anything gaseous. But, speaking generally, the basis of flame is a glowing gas, and the exciting cause chemical action. This description would include ordinary hot flames and also flames of the kind called phosphorescent, which may be quite cold in the ordinary sense of the word.

If, then, a chemical change takes place, resulting in the production of gas and the liberation of a quantity of latent chemical energy, a flame may make its appearance. Experience shows that this only occurs when the amount of energy liberated is very considerable, in other words, flames are only to be expected during the resolution of highly endothermic compounds, like guncotton, into gaseous constituents, or during the formation of highly exothermic compound gases from their components, as in the case of carbon dioxide from carbon monoxide and oxygen. In phosphorescent flames, such as that of phosphorus, the energy liberated per gram-molecule of product formed is no less considerable.

Flames produced during the decomposition of single endothermic compounds do not call for any detailed consideration, since, apart from their genesis, they do not present many special features of interest. The case of acetylene is interesting, inasmuch as a flame initiated in a column of the gas at one point is not propagated for more than a short distance, unless the gas is under a pressure of about two atmospheres.

Conditions determining flame. The principles underlying flame phenomena are best considered in the ordinary case where the flame is occasioned by combination between two substances, either single substances or mixtures of substances. Such a case as that of coal gas and air is complicated by the fact that both these substances are mixtures, and it is to be remembered that in the intermingling of such mixtures the diffusive power of each component will assert itself and lead, for the moment, to local variations of condition.

In selecting even one of the simplest cases for the purpose of discussing flame phenomena, it is necessary to premise that there are many factors of which we have at present only an imperfect knowledge, and many doubtless of which we have no conception at all. We may recall, for example, the remarkable discoveries concerning the influence of minute quantities of water vapour upon the initiation and intensity of combustion. The mechanism of what was formerly regarded as so simple a chemical phenomenon—the burning of hydrogen—is full of difficulties. H. B. Dixon, discussing this subject (Chem. Soc. Trans. 1910, 97, 661), considers that steam intervenes in the initial action of hydrogen on oxygen at moderate temperatures, but he does not think it necessary for the propagation of a flame once started in the mixture. The mode of action of the steam, which, according to E. W. Morley's calculation, quoted by Bone (British Association Reports, 1910), is present to less than the extent of 4 molecules per 1000 million molecules of dried gas, is at present unintelligible.

Notwithstanding Larmor's conclusion about the infrequency of trimolecular collisions in a gas, and the support thereby given to the theoretical and experimental inference of other workers as to the probability of one molecule of hydrogen uniting initially with one molecule of oxygen, Dixon shows that there are great difficulties in maintaining that hydrogen peroxide is the first product formed in a hydrogen flame.

Similar complications present themselves in nearly every case of combustion. The main phenomena of flame can, however, be usefully discussed without entering into minutiæ of the chemical transactions involved, and this course will be taken in what follows.

Limits of inflammability. In order that a flame of the common type may be produced, it is necessary to have the combining substances mixed in certain proportions, and to heat a portion of the mixture initially to a certain temperature. The proportions within which self-sustaining flame may be incited are called the *limits of inflammability*, and the temperature at which self-sustaining flame is set up is called the *temperature of ignition*.

When a portion of a stationary inflammable mixture is raised to the temperature of ignition, unless the quantity so heated is very minute, a flame travels through the mixture. The flame may, however, be quenched in the neighbourhood of surfaces of high heat conductivity, as, for example, when it enters narrow tubes or impinges upon a fine metallic meshwork. This is the well-known principle which applies in the miner's safety lamp, the flaming fire-damp and air within the lamp being extinguished in contact with the metallic gauze. The rate at which a flame travels through an inflammable mixture depends, apart from the form and material of the enclosure, on the nature of the gases, on their proportion in the mixture, and on the distance traversed. Formerly, the rates of inflammation of gaseous mixtures were supposed to be very moderate. Thus, for hydrogen and oxygen in the proportions of electrolytic gas, Bunsen gave the rate of propagation of flame as 34 metres per second.

The existence of vastly higher rates was first demonstrated by Berthelot, in the discovery of the 'explosive wave,' and as the result of his researches as well as those of Mallard and Le Chatelier and H. B. Dixon, we now know that in many gaseous mixtures the initial slow rate of *inflammation* may be succeeded by a rate of *explosion* or *detonation*, amounting to between 1500 and 3500 metres per second. If mixtures of this kind be ignited at the end of a long tube, the flame first proceeds with a sensibly uniform velocity for a distance of from 0·25 to 1 metre (period of inflammation); then a vibratory movement ensues, which increases in intensity until finally the explosive wave is set up, and the flame proceeds through the rest of the mixture with the high velocity just described.

In connection with flames, we are concerned only with the rates of inflammation, and these are exhibited for a number of mixtures in the diagram (Fig. 1 taken from Chapman, Chem. Soc. Trans. 1921, 119, 1679).

As will be seen from the diagram, the rate of propagation of flame is not necessarily greatest in mixtures containing the combining gases in the proportions just required for complete combination. The flame in a mixture of 40 p.c. of hydrogen and 60 p.c. of air has a higher rate of propagation than one with 28 or 29 p.c. of hydrogen (the stoichiometric proportions). This apparent anomaly is explained when we consider that (1) heat evolution per unit volume of the mixture diminishes as we depart from the stoichiometrical proportions: (2) heat conduction from layer to layer increases in rapidity as the proportion of the highly conducting gas (hydrogen) increases, until (3) this accelerating effect of the gas in excess is balanced by the diminution of heat evolved per unit volume of the mixture.

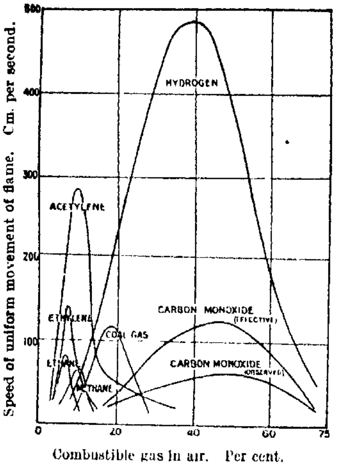


Fig. 1.

Temperature of ignition. The temperature of ignition of gaseous mixtures is the temperature to which a portion must be heated to produce self-sustaining flame. The fact that they are usually ignited by a match flame or a spark of high temperature produces the impression that a flame necessarily appears *per saltum*. Experiment and theory teach that the rate of chemical action varies continuously with varying temperature, and if flame is merely an accompaniment of chemical action, it should appear gradually as the temperature is increased. The fraction of combining molecules in a mixture at low temperature might not yield a visible amount of radiation; but as the temperature rose we might expect a glow to appear gradually and to intensify. As the rate of chemical action normally increases very rapidly with increasing temperature, the luminosity need not appear far below the temperature of ignition. To test this view, it is therefore necessary to examine mixtures in that region of temperature. Almost the only case that at once presents itself is that of phosphorus. Phosphorus ignites at about 60°, so that at the ordinary temperature it is within 50° of its temperature of ignition. The fact that its vapour glows at ordinary temperature is the best-known property of phosphorus. The glow diminishes as the temperature is reduced, and disappears at about 7°.

If other combustible substances are examined under corresponding conditions, the vast majority show the same property. All that is necessary is to heat them in admixture with air to a temperature near their igniting-point, when they show all the appearance of 'phosphorescence.'

When phosphorescence begins, the number of molecules combining in a given volume of the gas is small, so that the elevation of temperature of the whole mixture will be small. As the temperature is raised and the phosphorescence intensifies, a greater rate of combination has set in, and the liberation of heat becomes more perceptible.

The foregoing considerations lead to a tolerably precise characterisation of the temperature of ignition. As heat is supplied at an increasing rate to a gaseous mixture, the rate of combination increases, and if the combination itself produces heat, a point will be eventually reached when this heat will be produced with sufficient speed to compensate the loss due to radiation and conduction. The source of external heat may then be withdrawn and the burning will continue. The temperature required to induce this condition is the temperature of ignition. It may be well illustrated by causing the vapour of carbon disulphide to issue from a tube at the mouth of which is a ring of platinum wire that can be gradually heated by an electric current. A phosphorescent flame appears below the temperature of ignition. If the current through the platinum ring be diminished, the flame disappears; if it be raised, the flame increases in intensity until a certain temperature is attained when self-sustaining combustion ensues and accessory heat from the platinum ring is no longer necessary.

The following table of ignition temperatures is taken from a paper by Dixon and Coward (Chem. Soc. Trans. 1909, 95, 514):—

The Ignition Temperatures of Gases.

	Ignition temperature			
	In oxygen		In air	
	Between	Mean	Between	Mean
Hydrogen .	580°–590°	585°	580°–590°	585°
Carbon monoxide (moist)	637°–658°	650°	644°–658°	651°
Cyanogen .	803°–818°	811°	850°–862°	856°
Ethylene .	500°–519°	510°	542°–547°	543°
Acetylene .	416°–440°	428°	406°–440°	429°
Hydrogen sulphide . .	220°–235°	227°	346°–379°	364°
Methane .	556°–700°	—	650°–750°	—
Ethane . .	520°–630°	—	520°–630°	—
Propane .	490°–570°	—	—	—
Ammonia .	700°–860°	—	—	—

The gases were separately heated to the same temperature and then allowed to meet, and in this way certain difficulties attending earlier methods of determining ignition temperatures were overcome. Another method of determining temperatures of ignition employed by Falk (J. Amer. Chem. Soc. 28, 1517; 29, 1536) and modified by Dixon (Chem. Soc. Trans. 1910, 97, 674), consists in compressing the gaseous mixture under practically adiabatic conditions, and so heating it to the point of inflammation.

Types of flame. A stationary flame with complete combustion may be produced by igniting an inflammable mixture as it issues into a neutral atmosphere, or by allowing one of the combining gases to issue from an orifice into an atmosphere of the other, and igniting the self-made mixture at the orifice. A third method is to have one gas in excess in the mixture and to allow it to issue into an atmosphere containing the other. A[illegible] are found in practice, and they merge into each other. Let us consider the case of a flame of carbon monoxide in air, which lends itself readily to experimental demonstration. (*See* Fig. 2.)

If undiluted carbon monoxide be sent from a cylindrical tube under a gentle pressure, the flame which is formed is a simple hollow cone of blue light resting upon the orifice of the tube (*a*). If the tube be made of a material of high heat conductivity, there is a perceptible gap of extinction between the end of the tube and the superimposed flame. The genesis of the cone is easy to understand. The escaping gas makes its own mixture with air, and so the stream is burned through from the outside as it ascends. The current of gas, moreover, issues with a greater velocity in the axis of the tube than at the sides, where it is impeded by friction against the walls, and the unburned gas in the middle is also heated as it ascends through the burning walls. All these factors promote the conical form of the flame. The form of a carbon monoxide flame issuing from any other kind of orifice can be predicted from similar considerations. Of course, when the velocity of issue increases, the case is complicated by the turbulent motion of the gas.

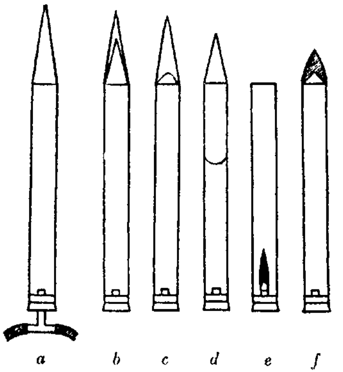


Fig. 2.

Let us now consider the effect of adding some air to the carbon monoxide before it issues from the orifice. Air added in this way is often called *primary* air, and the additional air taken from the atmosphere round the orifice to complete the combustion is called *secondary* air. A small quantity of primary air produces a noticeable effect upon the flame. The cone diminishes in height, and seems to have a lining of brighter blue (*b*). With a little more air, the lining is seen to be a second cone within the first, and consequently with a gentler slope. The individuality of this inner cone becomes apparent when the proportion of primary air mixed with the issuing gas is sufficient to bring the mixture well within the limits of 'inflammability' (*c*). The mixture is, indeed, inflaming downwards, but as the rate of propagation does not exceed the upward velocity of the gas stream, the inner cone of flame cannot travel against the gas stream. With more air, however, a greater rate of inflammation ensues, and eventually the inner cone, after becoming more and more squat, enters the tube and travels against the gas stream, first as a flat disc and then as a convex surface with the bulge downwards (*d*). Throughout all these changes, the second or outer cone is maintained at the orifice of the tube by the combustion in the external air of the carbon monoxide remaining in excess of what the primary air suffices to oxidise in the inner cone or disc. It loses in brilliance owing to its dilution with the carbon dioxide and nitrogen which come up from the inner cone. If the primary air supply be further increased, the outer cone will eventually disappear altogether, for a point is reached when the oxidation can be completed by the primary air (*e*). This, however, is not the end point, for an excess of primary air, just like a defect, diminishes the rate of inflammation, and consequently when this rate has been reduced below the velocity of outflow of the gaseous mixture, the single (inner) cone of flame will rise again to the orifice of the tube and remain there. It is to be noted that now the flame consists of only one film of burning gas. The film is still conical, in virtue of the greater axial velocity in the stream of gas, but it has considerable thickness, and its lower boundary is also a conical surface (*f*). There is need of a term to distinguish a flame of gas which is burning continuously throughout the whole or nearly the whole space included by its external surface, from one which is burning in thin films and whose external surface includes chiefly unburned gas. The word 'solid' is sometimes used in this connection, but a 'solid carbon monoxide flame' is obviously a contradiction in terms. Perhaps one might speak of a *volume flame* as distinguished from a *film flame*.

The last stage to be described in the development of the carbon monoxide air flame is reached when the excess of primary air brings the mixture near to the limits of inflammability, or, precisely speaking, when the rate of inflammation of the mixture is reduced below the velocity of the slow-moving part of the ascending gas mixture adjacent to the walls of the tube. The flame then gets detached from the orifice, rises, and disappears.

The various phases are shown diagrammatically in Fig. 2.

In Fig. 2 (*e*) the inner cone, which has retreated, is shown as being arrested at the orifice of the narrow tube through which the mixed gases are led into the wider one. The arrest is due to the fact that the velocity of efflux through the narrow tube exceeds in all cases, for the present example, the velocity of inflammation of the mixture. Mention may here be made of a piece of apparatus used by Smithells (Chem. Soc. Trans. 1892, 61, 204), known as the flame separator, as it depends for its action on the principle just referred to. The separator, Fig. 3, consists of two cylindrical tubes of different diameter, made preferably of fireproof glass, one of which slides within the other through an india-rubber collar. A brass candle adapter attached to the inner tube keeps the inner tube coaxial with the outer one. Mixtures of an inflammable gas and air can be admitted through the lower end of the narrow tube by attaching a T-piece, or more simply by attaching it to a Bunsen burner. In all cases, a two-coned flame can be obtained, and if the proportion of the gases is suitably adjusted for a velocity of inflammation intermediate between the upward velocity of the mixture in the wide tube and that in the narrow one, the inner cone will descend in the wide tube and come to rest at the orifice of the narrower one. If the outer cone be now slid down, a two-coned flame rests on the orifice of the narrow tube. The practical value of the appliance depends on the fact that it permits of the aspiration of the interconal gases in a pure state, and in this way it has been of assistance in the study of the progress of combustion in complex gases.

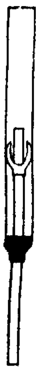


FIG. 3.

Flame temperatures. The principles developed in the discussion of the carbon monoxide air flame are applicable to all flames We may now apply them in connection with the question of flame temperature.

In speaking of the temperature of flame it is necessary to specify exactly what is meant by the term. Most flames are composed of thin films, and their external surface encloses a large quantity of unburned gas We might speak of the temperature of such a flame as meaning the average thermal state of the burning films and the included gas. This, however, is not the custom. The temperature attainable by the combustion of gas usually means the temperature which would be indicated by a thermometric instrument wholly immersed in the region of combustion. It is obviously very difficult to make such measurements in thin films of flame; in volume flames, produced by burning ready-made mixtures of combustible gas and air it is more practicable to measure the temperature experimentally. Flame temperatures have been measured chiefly (1) by exploding gaseous mixtures and calculating the temperature from the increase of pressure; (2) by means of thermo-couples, especially the platinum platinum-rhodium couple of Le Chatelier; (3) by use of optical pyrometers in cases where the flame contains incandescent solid; (4) by analysis of interconal gases and the application of thermodynamics. The subject, both theoretically and practically, is complicated, and an adequate discussion is impossible within the limits of this article. A 'theoretical temperature' of flame may be calculated from the thermal value of the reaction, and the mass and specific heat of the products. Thus, in the case of hydrogen, taking the heat of formation of a gram-molecule of steam (18 grams) to be 57,560 calories, and the specific heat of steam at constant pressure as 0·4805, we have:

$$\text{Rise of temperature} = \frac{57560}{18 \times 0{\cdot}4805} = 6655°.$$

As a matter of experiment, the temperature of an oxy-hydrogen flame is found to be about 2400° (Féry).

The discrepancy is easily understood, for the calculation involves several assumptions; the action is supposed to be instantaneous, so that no heat is radiated in the process, and the specific heat of steam is supposed to be unaltered at high temperatures. Both these assumptions are in conflict with experimental facts.

Calculated flame temperatures, where air is used, proceed on the assumption that the heat of reaction is distributed among all the products, including the passive nitrogen, so as to bring them to the same temperature. Thus, in the above calculation, we should, if air were used instead of oxygen, add a term for the nitrogen, &c., and so obtain a value of about 2500°.

Temperatures of flames, calculated in this way, for combustion in air, approximate more nearly to the measured temperatures, and the numbers obtained serve at least to give an estimate of the relative temperatures of different flames.

The following table is calculated by Le Chatelier, all the substances being burnt in air:—

C to CO_2 .	2040°	CH_4 .	1850°
C to CO .	1280°	C_2H_2 .	2420°
CO . .	2100°	Producer gas	1350°
H_2 . .	1970°		

To these may be added: combustion of C in air with 5 p.c. unused oxygen in the products, 1950°, ditto with 5 p.c. of CO in the products, 1930°; producer gas with air supply heated to 1000°, 2150°.

How far these calculated figures accord with direct measurements may be illustrated by the following results, given by Féry, who used an optical method:—

MAXIMUM FLAME TEMPERATURES (FÉRY, 1904).

	Deg. C.	Deg. F.
Bunsen burner, gas fully aërated	1871	3400
,, ,, insufficient air	1712	3114
Acetylene flame . . .	2548	4618
Alcohol flame	1705	3101
Denayrouze burner, alcohol and air	1862	3384
Do., half each alcohol and petroleum spirit	2053	3727
Hydrogen, free flame in air .	1900	3452
Oxy-coal gas blow-pipe flame .	2200	3992
Oxy-hydrogen ,, ,, .	2420	4388

To these may be added a series of recorded temperatures of the flame of a Bunsen burner using coal gas:

MAXIMUM TEMPERATURE IN THE FLAME OF A BUNSEN BURNER USING COAL GAS.

Date.	Deg. C.
1860.—Bunsen and Kirchhoff . .	2350
1877.- Rosetti	1360
1892.—Rogers	1230
1892.—Lewes	1630
1895.—M'Crae	1725
1896.—Waggener	1770
1899.- Berkenbusch . . .	1830
1902.—White and Traver . .	1780
1905.—Féry	1871

Only the later numbers are of importance. Féry estimates the temperature of the electric arc to be 3760°, and that of the sun to be 7800°. The temperature of the acetylene-oxygen flame is supposed to be between 3000° and 4000°.

Another aspect of the temperature question presents itself when the practical use of flames is involved. As an example, we may briefly discuss the use of a coal-gas air flame for heating a Welsbach mantle. The object is, of course, to get the mximum flux of light from the consumption of a fixed amount of coal gas, in other words, we seek to raise the maximum mantle [illegible] maximum temperature. A primary consideration is, that as the temperature is raised the intensity of light emitted increases in a much more rapid ratio. The total energy radiation of an ideally 'black body' increases as the fourth power of the absolute temperature, and of this radiation the proportion which is visible also increases in a rapid ratio. This is especially the case with the Welsbach mantle which has a selective radiating power for short wave lengths. Even a small reduction in temperature must therefore be accompanied by a loss of intrinsic brilliance.

Again, having regard to the shape of a mantle, to its inevitable irregularities, original or acquired, and to the unsteadiness of a flame, it is evident that a high temperature can only be attained when it is suspended in a tolerably thick stratum of flame, although the mantle has doubtless a steadying and localising effect on the flame.

Reverting to the discussion of the carbon monoxide air flame we may easily apply the conclusions to the case of a Bunsen burner, using coal gas and air. This burner, as used in its ordinary form, draws in through the air ports at the base (by the injector action of the coal gas escaping from the nipple) from 2 to 2½ times its volume of air, about half the amount required for complete combustion. This air effects a partial oxidation of the coal gas, and yields an inner cone of flame; the oxidation is completed when the products from the inner cone mingle with the external air, an outer cone being formed. A Bunsen or 'atmospheric' burner thus gives a double flame. If the two cones be separated by a considerable interval in the flame separator, it is easy to show that the temperature reigning in the inner cone exceeds that in the outer cone, but if the two cones are close together, the reverse is the case. The explanation is to be found in the fact that when the two cones are near, the gases coming to the outer cone have still a high temperature from the act of their formation, and their temperature is to be added to the rise occasioned by the completion of their combustion, in the outer cone. From this it might appear that the best disposition of a mantle in the flame would be that in which it occupies the surface of the outer cone. But it is to be remembered that the mantle deforms the cone by altering the currents of gas and air, and, besides, the outer surface of the mantle will lose heat very rapidly if it is at the confines of the flame. We should rather suppose, therefore, that it would be better to submerge the mantle in the flame to some extent, and if this is done and if at the same time by the use of a glass chimney we cause a more rapid flux of air round the flame to quicken the combustion in the outer cone, we get the conditions which, as a matter of fact, have been found most effective for heating a mantle with the original type of Bunsen burner.

The great gain to be secured by raising the temperature of the mantle soon led to modifications of the original Bunsen burner, whereby it was sought to introduce a larger proportion of primary air. A large number of devices have been used, of which the two most important relate to the form of the burner tube and to the construction of the burner head.

In the well-known Kern burner, the tube formed on the Venturi principle, and has i ternally the form of a hyperbolic spindle A. Th secures an intake of primary air which is pract cally sufficient for complete combustion. Th mixing of air and gas and the stability of th flame are secured by an expanded burner hea capped by a serrated disc B, through the teeth which the gas mixture issues in narrow stream These streams coalesce and produce a conic sheet of flame of uniform character and sensib thickness. The flame, in fact, is of the blow pipe type (Fig. 4A).

The Méker burner is constructed on muc the same principle, but the gas mixture pass from the expanded burner head through a de metal grid. The flame is therefore a cone gas burning through and through. It will seen that the Kern flame is designed special for heating a mantle, whilst the Méker flame designed to confine the combustion to the sma est attainable volume and to provide a ve compact hot flame for general laboratory furnace use (Fig. 4B).

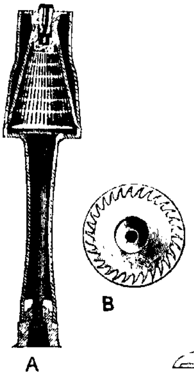


FIG. 4A.

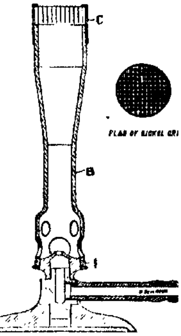


FIG. 4B.

Increased in-draught of air can also secured by the use of chimneys. If the gas air or both are put under extra pressure and delivered with high velocity, volume flames m be obtained, which, unlike that of a Mék burner, have their base blown up into a con so that the flame appears to be two-coned. Th really constitutes a blowpipe flame.

The inversion of a Bunsen flame modifi its form in such a way as to make it mo efficient for heating a mantle. The outer fi of flame becomes shorter, thicker, and mo globular, and as the products of combusti necessarily drift back past the flame, there a certain recuperation of heat.

The efficiency of various flames for givi light may be gathered from the followi table of illuminating value per cubic foot gas consumed. The numbers are, of cours only approximate, but they give an idea the temperatures to which the mantle is raise The fact that in all cases the same chemic action is taking place shows how misleadi the term 'flame temperature' may be unle the precise character and use of the flame are specified :—

Form of burner	*Candle-power per cubic foot consumed*
Ordinary batswing	2·5
Argand	3·25
Wenham (regenerative)	8–9
Upright, with mantle	20–40 (according to pressure)
Inverted ,,	20–70 ,, ,,

The hottest flame that is in practical use is that of the acetylene-oxygen blowpipe. In this case, we have not only the heat of oxidation of the carbon and hydrogen involved, but also the positive heat of decomposition of the molecule of acetylene. The acetylene-oxygen flame can be used for welding iron and also for perforating steel. (*v.* Acetylene; Oxygen.)

The chemical changes taking place in flames. In the foregoing part of this article, attention has been drawn to general principles which are applicable to flames as a whole, without particular regard to the detailed features of structure or the stages of chemical decomposition. Before discussing any flame in particular, we may adduce one or two further general considerations with regard to chemical changes in flame. It has been assumed, for the sake of simplicity, that in the flames of hydrogen and carbon monoxide the chemical change takes place in one simple step. When we come to other combustibles, it is obvious that such assumptions may be still less warrantable. If, for example, we are dealing with a combustible element which is capable of affording two oxides, we may have the oxidation in the flame taking place in two stages, each stage producing a distinctive feature in the flame. Or, if we have a combustible consisting of two or more oxidisable elements, the oxidation might conceivably take place selectively. Again, in a compound combustible, it is possible that the oxygen may, in the first instance, add itself to the molecule of combustible, producing a complex substance which is ultimately resolved. Lastly, it is possible that the heating effect of the burning envelope in a flame may produce a purely thermal chemical effect on some of the enclosed unburned gas.

Only in a few cases has the progressive combustion in flames been studied fully. In the case of a cyanogen-air flame, it has been shown (Smithells and Dent, Chem. Soc. Trans. 1894, 65, 603) that the inner crimson film of the flame marks the combustion of the gas to carbon monoxide, whilst in the blue fringe of the flame the oxidation is completed by the combustion of the carbon monoxide.

The case of hydrocarbon flames is naturally the one of most interest. The earliest investigations of the progress of combustion, made by Hilgard, Landolt, and Blochmann, in Bunsen's laboratory, dealt with the flames of the complex combustibles, wax, vegetable oils, coal gas, and consequently the results were not very easy to interpret. In more recent times, the combustion of single hydrocarbons has been carefully examined.

The flame of a hydrogen-carbon compound, or of a mixture containing some quantity of hydrocarbons, shows three distinct parts when produced in the ordinary way. Of these, the most conspicuous is the bright yellow patch from which the chief flux of light takes place. The lower part of the flame is surrounded by a bright-blue sheath or 'calyx,' which thins off and ends where it overlaps the lower part of the yellow region. In addition to this, the whole flame is surrounded by a complete mantle of dimly burning gas. The flame is hollow, that is to say, it is filled with unburnt gas, and even the bright-yellow region is an extremely thin conical sheet. A diagrammatic section of a normal hydrocarbon flame is given in Fig. 5

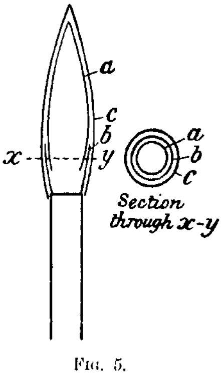


Fig. 5.

The relative development of the different parts is, of course, different in different flames. It depends on many factors, the chief of which are the richness of the gas in carbon, the character of the orifice, and the rate at which the gas issues. The flame of acetylene, suitably developed by allowing the gas to issue in such a way that it is spread out into a thin sheet, shows a very large yellowish-white luminous region, in the glare of which the other parts of the flame are indistinguishable. On the other hand, an alcohol flame exhibits scarcely any yellow luminosity.

If we take the flame of a hydrocarbon burning in an ordinary Bunsen burner with the air ports closed, and then gradually open the ports, we can see how the luminous flame passes into the 'atmospheric' type, and convince ourselves that the blue calyx and the mantle of the luminous flame represent respectively the inner and outer cones of the Bunsen flame. Turning a luminous flame low to the point where only a blue button of light remains at the burner tip, enables us to see a like transition.

The changes experienced by hydrocarbons when burning in a Bunsen burner were investigated by Smithells and Ingle by the use of the cone-separating apparatus already described (Chem. Soc. Trans. 1892, 61, 209), and the analyses of the interconal gases (after cooling) showed in all cases that a partial combustion had taken place, leaving very little of the original hydrocarbon unoxidised. The products of partial oxidation were carbon monoxide, carbon dioxide, hydrogen, and water vapour, accompanied, of course, by the nitrogen of the 'primary' air supply. The following are some of the analytical results :—

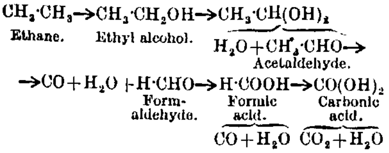
Gas employed.	C_2H_4	CH_4	C_6H_6	Coal gas
CO_2 . .	3·6	6·8	13·1	4·2
H_2O . .	9·5	17·6	7·7	16·0
CO . .	15·6	4·5	5·0	8·8
Hydrocarbon	1·3	—	0·6	—
H_2 . .	9·4	3·9	0·6	9·3
N_2 . .	60·6	67·2	73·1	62·0

These analyses refer to the cooled gases, but experiments (unpublished), made by a modification of Deville's method to entrap and preserve the gases as they exist at the high temperature, have not given any ground for doubting that the figures given in the table represent essentially the changes that occur in the inner cone. Independent experiments by Haber and Richardt (Zeitsch. anorg. Chem. 1904, 38, 5) bear out this conclusion.

We may say, therefore, that the inner cone of a Bunsen flame (and the corresponding blue calyx of a luminous flame) marks the region of a partial oxidation in which no carbon, but some hydrogen, remains unoxidised. In the outer cone (and the corresponding mantle of a luminous flame), the carbon monoxide and hydrogen coming from the inner cone (or calyx) find, and are burning with, the air necessary to complete their oxidation.

The experimental results just described stood in direct opposition to a view which, notwithstanding repeated contradictory evidence, had prevailed for three-quarters of a century, namely, that in the combustion of a hydrocarbon with a deficiency of air, the hydrogen was preferentially or selectively oxidised, and the carbon set free. It might now be said that there is a preferential or selective combustion of the carbon. The use of these expressions has, however, been objected to, and need not be insisted upon. The objection arises chiefly from a consideration of the results obtained by a long and careful series of studies made by W. A. Bone and his collaborators, on the progressive oxidation of hydrocarbons from a temperature of 250° upwards. The results of these experiments are summarised in a Report on Gaseous Combustion, drawn up by Professor Bone for the British Association (*see* B. A. Report, Sheffield, 1910), and in this report references to the original papers will be found. According to Bone, 'the attack of the oxygen upon the hydrocarbon may be supposed to involve a series of successive "hydroxylations," the hydroxylated molecules either breaking down or undergoing further oxidation, according to their relative stabilities and affinities for oxygen at the particular temperature.' The following is the scheme for ethane :—

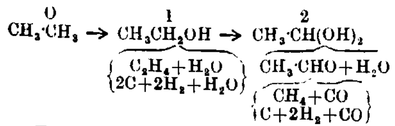
(*a*) SLOW COMBUSTION AT 300°–400°.



$$\underset{\text{Ethane.}}{CH_3\cdot CH_3} \rightarrow \underset{\text{Ethyl alcohol.}}{CH_3\cdot CH_2OH} \rightarrow \underbrace{CH_3\cdot CH(OH)_2}_{H_2O+\underset{\text{Acetaldehyde.}}{CH_3\cdot CHO}\rightarrow}$$

$$\rightarrow CO+H_2O+\underset{\text{Formaldehyde.}}{H\cdot CHO} \rightarrow \underbrace{\underset{\text{Formic acid.}}{H\cdot COOH}}_{CO+H_2O} \rightarrow \underbrace{\underset{\text{Carbonic acid.}}{CO(OH)_2}}_{CO_2+H_2O}$$

(*b*) EXPLOSIVE COMBUSTION.



$$\overset{0}{CH_3\cdot CH_3} \rightarrow \underbrace{\overset{1}{CH_3CH_2OH}}_{\begin{Bmatrix}C_2H_4+H_2O\\2C+2H_2+H_2O\end{Bmatrix}} \rightarrow \underbrace{\overset{2}{CH_3\cdot CH(OH)_2}}_{\underbrace{CH_3\cdot CHO}_{\begin{Bmatrix}CH_4+CO\\C+2H_2+CO\end{Bmatrix}}+H_2O}$$

The experimental basis of these schemes lies in the actual isolation of the various members of the series of transition substances implicated.

Space allows of only one further reference to these investigations. Bone considers that one of the most significant features 'has been the proof afforded of the relatively much greater affinity of hydrocarbons as compared with that of either hydrogen or carbon monoxide, for oxygen at the high temperature of flames.' Thus in the explosion of a mixture corresponding to $C_2H_4+H_2+O_2$ there is practically no formation of steam.

Luminosity of hydrocarbon flames. In the preceding paragraphs, the chemistry of the combustion of hydrocarbons in the Bunsen flame and in the blue parts of luminous flames has been explained in its general features. It remains to explain the development of the yellow luminous region of hydrocarbon flames. As is well known, the first explanation was given by Humphry Davy, in 1816, among many other observations upon flame still well worthy of attention. Davy attributed the luminosity to the deposition of solid charcoal, which he said 'might be owing to a decomposition of a part of the gas towards the interior of the flame where the air was in smallest quantity.' The ambiguity of this explanation and its supposed implication of a selective combustion of the hydrogen, have already been alluded to. Starting from this 'solid particle' explanation of the light of a hydrocarbon flame, Davy was led to consider that all flames of high luminosity contained solid particles. He knew that the phosphoric oxide was gasefied at the temperature of a phosphorus flame, yet he believed that, in the flame itself, solid particles of the substance were produced, and were conserved by the elastic force of the flame producing a kind of compression.

Davy's explanation remained unassailed until 1867, when E. Frankland made an important series of researches on the luminosity of flames. He concluded :

(1) That bright flames exist which do not contain solid particles.

(2) That the luminosity of flames depends mainly on the density of the substances contained in them.

(3) That feebly luminous flames may be made bright by compressing the burning gases.

(4) That the luminosity of ordinary hydrocarbon flames, such as that of coal gas, is not due, in any important degree, to solid particles of carbon, but almost entirely to the glow of dense hydrocarbon vapours.

Frankland attributed luminosity to the density of the hot gases in the flame, whether this density were due to high molecular weight or to compression. So far as hydrocarbon flames are concerned, Frankland's views were soon submitted to destructive criticism, especially by Heumann.

A crucial experiment indicating the presence of solid particles in flame, first proposed by Soret and subsequently by Burch and by Stokes, consists in focussing the image of the sun on to the flame and examining the scattered light with a Nicol prism. That test, applied to a hydrocarbon flame, gives a positive result, and the presence of solid particles in such flames is no longer disputed.

It is true that the black soot deposited on cold objects introduced into luminous hydrocarbon flames is by no means pure carbon, but this is to be expected when we remember that any condensible hydrocarbon in the flame would be deposited along with particles of pure carbon, if such were, in fact, present.

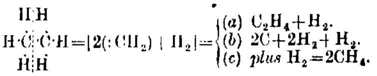
It may now be taken as agreed that the luminosity of hydrocarbon flames is due to the separation of solid particles of carbon. The process by which the carbon becomes separated in the flame has been the subject of much experiment and discussion. Is it involved directly in the oxidation that is taking place, or is it merely a thermal effect—and in either case, what are the stages of the process? It is impossible here to give more than a brief summary of the views that have been held. In the first place, it may be said that the old, simple, and plausible explanation of a preferential oxidation of hydrogen is untenable for reasons already given. In the next it may be affirmed that, generally speaking, hydrocarbons, subjected to a high temperature, deposit solid carbon. It would appear, therefore, that the separation of carbon in a flame might be adequately explained by the fact that the unburned hydrocarbon within the burning sheath of the flame is highly heated by the burning parts. The fact that when the heat is tapped for the burning sheath by a ring of cold wire, the flame loses luminosity, is one among several indications that the deposition of carbon is a secondary and a thermal effect of the combustion. At the same time, the experiments of Bone would lead us to be cautious in denying that in some cases the chemical processes might contribute to the separation of carbon.

Taking it for granted that the decomposition of the hydrocarbon is purely thermal, we may next consider the stages that are passed through. This raises the whole question of the thermal decomposition of hydrocarbons, a subject of great experimental difficulty, on which really satisfactory results have only been obtained over a small range of substances (*see* Bone and Coward, Chem. Soc. Trans. 1908, 93, 1197).

The view that ethylene, on heating, undergoes the simple change $C_2H_4=C+CH_4$, which long served to explain the luminosity of flames, is no longer tenable. The doctrine of Berthelot, according to which the molecules of hydrocarbons, on heating, undergo progressive coalescence with elimination of hydrogen until in the end a molecule is left containing a negligible proportion of hydrogen, is likewise contradicted by modern experiments. The hypothesis of V. B. Lewes (Proc. Roy. Soc. 1895, 57, 450), that the formation of acetylene and its subsequent decomposition are the essential cause of luminosity in hydrocarbon flames, is regarded by those who have concerned themselves with the subject as based on wholly insufficient evidence.

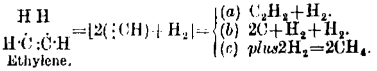
Bone and Coward have been led to the conclusion that the thermal decomposition of hydrocarbons is too complex a phenomenon to be represented by ordinary chemical equations. Dealing with methane, ethane, ethylene, and acetylene, they observe first of all that whilst at a high temperature methane, the most stable of the hydrocarbons, is resolved directly into carbon and hydrogen, this only takes place in contact with solid surfaces, whilst with the three other gases decomposition takes place throughout their bulk.

They say: 'In the cases of ethane and ethylene, it may be supposed that the *primary* effect of high temperature is to cause an elimination of hydrogen with a simultaneous loosening or dissolution of the bond between the carbon atoms, giving rise to (in the event of dissolution) residues such as : $:CH_2$ and $\vdots CH$. These residues, which can only have a very fugitive separate existence, may subsequently either (*a*) form $H_2C\!:\!CH_2$ and $HC\vdots CH$, as the result of encounters with other similar residues, or (*b*) break down directly into carbon and hydrogen, or (*c*) be directly "hydrogenised" to methane in an atmosphere already rich in hydrogen. These three possibilities may all be realised simultaneously in the same decomposing gas in proportions dependent on the temperature, pressure, and amount of hydrogen present. The whole process may be represented by the following scheme, the dotted line indicating the tendency to dissolve the bond between the carbon atoms which becomes actually effective at higher temperatures :—



$$\begin{matrix}H & \vdots & H \\ H\cdot\dot{C} & \vdots & \dot{C}\cdot H \\ \dot{H} & \vdots & \dot{H}\end{matrix} = [2(:CH_2)+H_2] = \begin{cases}(a)\ C_2H_4+H_2.\\(b)\ 2C+2H_2+H_2.\\(c)\ plus\ H_2=2CH_4.\end{cases}$$

Ethane.



$$\begin{matrix}H\ \ H \\ H\cdot\dot{C}\,\vdots\,\dot{C}\cdot H\end{matrix} = [2(\vdots CH)+H_2] = \begin{cases}(a)\ C_2H_2+H_2.\\(b)\ 2C+H_2+H_2.\\(c)\ plus 2H_2=2CH_4.\end{cases}$$

Ethylene.

'In the case of acetylene, the main primary change may be either one of polymerisation or of dissolution, according to the temperature, and, if the latter, it may be supposed that the molecule breaks down across the triple bond between the carbon atoms, giving rise to $2(\vdots CH)$, and that these residues are subsequently either resolved into carbon and hydrogen or "hydrogenised," according to circumstances, thus :

$$HC\underset{\downarrow}{\vdots}CH=2(\vdots CH)=\begin{cases}(a)\ 2C+H_2.\\(b)\ plus\ 3H_2=2HC_4.\end{cases}$$

Polymerisation.

'Incidentally, it may be observed that the rates of decomposition of these hydrocarbons are very much slower than their rates of combustion, and that therefore in the propagation of a flame through a homogeneous mixture of a hydrocarbon and oxygen, oxidation will probably take precedence of all other chemical phenomena.'

The chemistry of a hydrocarbon flame has now been given as completely as present knowledge and the limits of space allow.

The art of getting the maximum of light from a hydrocarbon solely by its own combustion may be deduced and stated briefly as follows: The gas must be so burned as to liberate within the burning walls of its flame the maximum amount of solid carbon that can be heated to a high temperature and be wholly oxidised as well. Spreading out the gas stream increases the relative proportion of hot non-luminous burning walls, and diminishes the central zone of unburned gas from which the solid carbon has to be derived. It is on the right adjustment of these two elements of a flame for the particular gas in use, that the construction of a suitable burner depends, and it is obvious that the best result can only be maintained when the composition of the gas and air, the pressure, and temperature are kept constant. Of course, the question is complicated when we introduce the factors of chimneys and heat-regenerating devices.

It may be convenient here to revert to the question of obtaining the highest temperature from the combustion of a fixed amount of a hydrocarbon. Fig. 6 is reproduced from photographs of five gas-flames, where the rate of gas flow was constant. In the first flame, A, we have the gas burning (with some smoke) without any 'primary' air [1]; in the second, we have just sufficient primary air to cause delumination; in the third, we have as much air as possible without producing instability; in the fourth, a Méker burner is used; in the fifth, we have the gas mixed, before issuing from the burner, with enough carbon dioxide to produce delumination. Speaking of each flame as a whole, we may say that the hotness is greater in proportion as the surface is less. In the carbon dioxide-fed flame, neutral molecules of that gas are wedged in between those of the combustible gas, and the mixture has to wander far before it gets mixed with enough oxygen to sustain combustion. When it acquires this oxygen, there is round each burning molecule not only the inert nitrogen of the air but the equally inert carbon dioxide. The flame is a thin, single, hollow sheet, and the temperature is quite insufficient to decompose any of the hydrocarbons within. It has the non-luminous appearance of a Bunsen flame, but it is, of course, absolutely the opposite of that in its genesis, for it represents delayed and diluted instead of quickened and concentrated combustion.

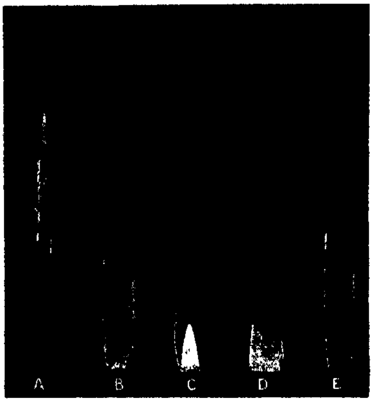


Fig. 6.

The limits of space have rendered necessary the omission of many matters relating to the chemistry and physics of flame. The exact molecular and sub-molecular mechanism by which the luminosity of wholly gaseous flames is regulated, is a subject of great interest. It is now generally believed to be associated with electronic transactions. Some discussion of the subject is to be found in the British Association's Report, Leicester, 1907 (Smithells' address to Section B). A. Sm.

FLASH LIGHTS. A term usually applied to combustible mixtures which burn with a brilliant light and more or less instantaneous flash, and which are employed specially for photographic purposes. Slower-burning mixtures, which also yield a bright light on combustion, such as are used for signalling purposes, are known as *flares* (*see* BENGAL LIGHTS; INDIAN FIRE; PYROTECHNY).

For photographic purposes, it is essential that the flash light should be (1) sufficiently brilliant, (2) of the desired rapidity, and (3) specially rich in actinic light. Of all the known available materials which, on combustion, yield a bright and highly actinic light, the metal magnesium stands pre-eminent; and the earliest and simplest methods of employing this substance consisted in projecting a definite quantity of the finely powdered metal into the flame of a spirit lamp.

Various contrivances have been devised for this purpose: one simple plan is to place the charge of magnesium powder in the bowl of a clay tobacco pipe to the mouthpiece of which is attached a rubber ball. A loose plug of tow or cotton wool, wetted with methylated spirit, is then lightly inserted into the mouth of the bowl: the spirit is ignited and, on suddenly squeezing the ball, the magnesium is thrown into the flame.

The next development consists in mixing the powdered magnesium with some highly oxygenated salt, such as potassium chlorate, in such proportion that the mixture, when placed in a small heap upon a metal tray, could be ignited by a match or taper, and would burn with much the same rapidity as a similar small heap of gunpowder. The danger inherent in such mixtures was found to be greatly reduced by substituting barium chlorate for the potassium salt; and more recently, since potassium perchlorate has become a common commercial article, this compound is more usually employed in preference to the chlorates.

Mixtures of magnesium with certain nitrates of the so-called rare earths have been made the subject of patents. One such consists of:

Magnesium powder	10 parts
Thorium nitrate	10 ,,

and a rather less quick mixture contains:

Magnesium powder	10 parts
Zirconium nitrate	5 ,,

One of the chief drawbacks to magnesium flash powders is the volume of white smoke of magnesium oxide which is produced on their combustion, and many efforts have been made to obviate this nuisance. Some of these are purely mechanical contrivances for withdrawing the smoke, but others are attempts to produce mixtures which shall emit little or no smoke.

The two following mixtures claim to yield smokeless magnesium flash powders:—

(1) Powdered magnesium, barium peroxide, and collodion. The charge of powder is blown by means of a pneumatic pump into a small iron crucible heated by a Bunsen burner.

(2) 1 part of magnesium powder mixed with 1 part of either silicic acid ('infusorial earth'),

---

[1] The unsteadiness of this flame makes it appear somewhat too large in a photograph.

barium sulphate, anhydrous calcium sulphate, anhydrous magnesium sulphate ('kieserite'), or boric acid.

It is further claimed for this mixture that if loaded into a cylindrical case with a constricted opening, a non-instantaneous or 'time' flash may be obtained.

At the present time, since the pyrotechnic possibilities of finely powdered aluminium have become known, in most flash powders the magnesium is usually more or less replaced by aluminium, in some cases even wholly replaced; one such mixture consists of:

Aluminium powder .	40 parts
Potassium perchlorate .	60 ,,

It is usual, however, to retain some of the magnesium in order to ensure the necessary high actinic quality of the light emitted. Thus a typical mixture consists of:

Powdered magnesium .	100 parts
Powdered aluminium .	50 ,,
Ferric oxide . . .	30 ,,
Copper carbonate . .	30 ,,
Magnesium sulphate (dry)	5 ,,

The following mixtures claim to be non-explosive and almost smokeless:—

(1) Powdered magnesium and aluminium (the quantity of aluminium usually varying from $\frac{1}{4}$ to $\frac{1}{2}$ the amount of magnesium), mixed with peroxides of calcium, magnesium, or manganese.

(2) Powdered magnesium and aluminium mixed with perboric acid or tungstic acid or their salts.

(3) Powdered magnesium and aluminium, with sulphate of cerium or thorium, or an alum. For example:

Powdered magnesium . . .	8 parts
Powdered aluminium . . .	2 ,,
Finely powdered, dry chrome alum	10 ,,

Many mixtures containing aluminium as an ingredient are rendered more rapid in their combustion by the addition of silica, while their rate of combustion may be retarded by the introduction of regulated quantities of carbonates of alkalis or alkaline earths or oxides of the latter. Thus the above mixture may be converted into a slow-burning 'time' mixture by the addition of 2 parts of an alkaline earth oxide or carbonate.

Flash powders are now frequently loaded into small cases or cartridges; ignition of the mixture being effected sometimes by an electric arrangement and sometimes by means of an inserted strip of magnesium ribbon. In the former case, the two electric wires are fixed into the cartridge, with either a short spark-gap or joined by a fine incandescing wire.

One of the many patented cartridges has a case which is itself inflammable. It consists of a short celluloid cylinder closed at the bottom with a cork saturated with collodion, and at the top with a disc of cork saturated with an emulsion of magnesium. Through this, there is inserted a short strip of magnesium ribbon which, on ignition, communicates its combustion to the charge.

A number of contrivances have been devised for producing a rapid succession of flash lights for purposes of cinematograph photography. These consist essentially of mechanical devices for the intermittent feeding of metallic magnesium against the two metal terminals of an electric circuit. G. S. N.

FLAVANILINE *v.* QUINOLINE.

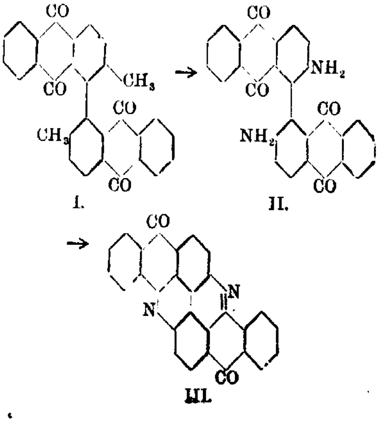
FLAVANTHRENE $C_{28}H_{12}O_2N_2$ An anthracene dyestuff discovered by R. Bohn of the Badische Anilin- und Sodafabrik, by melting β-aminoanthraquinone with caustic potash. Has a large application for unmordanted vegetable fibres, which assume a deep-blue colour in the reduced vat, changing after a few minutes' exposure in the air to a permanent yellow. The colour is very fast, except when subjected to powerful rays of sunlight, which cause it to assume a temporary green shade.

Prepared technically from 2-aminoanthraquinone and potassium hydroxide at 350° (D. R. P. 133686); with aluminium chloride (D. R. P. 136015); with antimony pentachloride in boiling nitrobenzene (D. R. P. 138119); by oxidising with chromic acid or other acid oxidising agents (D. R. PP. 139633 and 141355); in the last-named case, it is accompanied by indanthrene, to which it is closely related (*v.* INDANTHRENE).

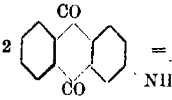
Flavanthrene is a weak base, sparingly soluble in high-boiling solvents, and very stable towards heat; it exists in glistening, brown-yellow needles. It is applied to the fibre after reduction with alkaline hyposulphites, forming a deep-blue vat (D. R. PP. 139634, 139835, 140573, 142963).

The constitution of flavanthrene has been determined by R. Scholl and his co-workers (Ber. 1907, 40, 1691) in the following manner:—

1-amino-2-methylanthraquinone was converted by the diazo- reaction into 1-iodo-2-methylanthraquinone $C_{15}H_9O_2I$, which passes by means of Ullmann's copper method (Annalen, 1904, 332, 38) at 270° into 2:2′-dimethyl-1-dianthraquinonyl (I.). This substance has also been prepared from the diazonium sulphate of the methylanthraquinone by means of copper powder and acetic anhydride (Knoevenagel, Ber. 28, 2048), and, when oxidised with chromic acid, yields the corresponding dicarboxylic acid $C_{30}H_{14}O_8$. The acid-amide derivative was readily obtained from this in the ordinary way, and the application of Hofmann's reaction with bromine and potash converts it into the amine (II.) and a stage further into flavanthrene (III.).



Flavanthrene must therefore have the annexed constitution III., and in obtaining it from 2-aminoanthraquinone in the process of manufacture, two molecules must unite with loss of two molecules of water and two atoms of hydrogen, according to the scheme :



$$= \underset{\text{Flavanthrene.}}{C_{28}H_{12}O_2N_2} + 2H_2O + H_2$$

The immediate precursor of flavanthrene, 2 : 2′-diamino-1 : 1′-dianthraquinonyl may be prepared by boiling 1-chloro-2-benzylidene-aminoanthraquinone with copper powder and naphthalene, extracting the 2-2′-dibenzylidene-amino-1 : 1′-dianthraquinonyl so formed with cold alcohol, and leaving the solution for some time, when the benzylidene residues are spontaneously eliminated and the desired compound crystallises. It forms microscopic red needles, and changes into flavanthrene at 250° (Scholl and Dischendorfer, Ber. 1918, 51, 452 ; Chem. Soc. Abstr. 1918, 308).

As the application of this dyestuff to the fibre depends upon its behaviour towards reducing agents in the vat, just as in the analogous case of indigo, careful investigations have been carried out by R. Scholl and his assistants (Ber. 1908, 41, 2304), under a variety of conditions, which show that the reduction products of flavanthrene consist of some seven definite compounds :

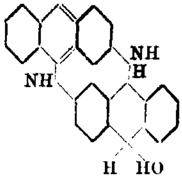
(*a*) *Dihydroflavanthrene hydrate*, obtained by reducing flavanthrene with alkaline sodium hyposulphite in an atmosphere of hydrogen. On cooling, bronze-coloured needles of the disodium salt of this hydrate crystallise out, and by acidifying with acetic acid, the free dihydroflavanthrene hydrate is isolated as bluish-green coppery crystals, which remain stable at the ordinary temperature, but readily oxidise to flavanthrene at 100° or when moist.

(*b*) *Dihydroflavanthrene* is obtained from the above by dehydration at 150°–170° in a stream of carbon dioxide ; it consists of a green powder which is more stable than the hydrate. It may also be prepared by reducing flavanthrene with hydriodic acid and red phosphorus at 125°. Although flavanthrene itself is only a weak base, this dihydro derivative readily forms salts with mineral acids ; dihydroflavanthrene hydrochloride probably contains the acid united to a N- atom. The *o*-benzoyl derivative melts at 220°.

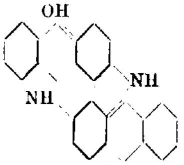
(*c*) *a-Tetrahydroflavanthrene hydrate* is isolated in the form of its sodium salt when flavanthrene is reduced with zinc-dust and caustic soda. On acidifying, (*a*) and (*f*) are formed.

(*d*) *Flavanthrine hydrate*, prepared by reducing flavanthrene with hydriodic acid and red phosphorus at 210°, is a greenish-brown powder, losing water at 240° with formation of *flavanthrine*, which consists of large brown needles with a metallic lustre, m.p. 30°. It is readily oxidised to flavanthrene.

(*e*) *a-hexahydroflavanthrene*, and (*g*) *Flavanthrinol*, are both formed by energetic reduction of flavanthrene with zinc-dust and caustic soda.



(*f*)



(*g*)

(*f*) is a stable blue-black powder which loses water at 160° ; dissolves in alcohol to a bluish red solution with a brilliant scarlet fluorescence. It forms fluorescent solutions in alcoholic alkalis and concentrated acids, dyeing unmordanted wool in the alkaline bath red, which changes to greenish blue with acids and violet on washing with water. Prolonged heating of the hydrate of (*f*) with zinc-dust in alkaline solution converts it into the hydrate of (*g*), whilst the anhydrous compound itself, (*f*), is further dehydrated at 300° in carbon dioxide, with formation of anhydrous flavanthrinol (*g*). By means of a current of air, an alkaline solution of (*f*) readily passes into flavanthrene.

Flavanthrinol (*g*) may be obtained from its hydrate by heating to 160°, and forms red solutions with an olive-green fluorescence in concentrated acids, and dyes unmordanted wool violet-red, becoming green with acids and blue with water. Flavanthrinol requires to be heated in air or oxidised with ferricyanide before it will yield the original flavanthrene.

Another method of obtaining flavanthrene, though only in small yields, is described below (Scholl, Ber. 1910, 43, 1734). Dianthraquinonyl, on nitration, forms a mixture of dinitro derivatives, which by reduction with sodium sulphide give flavanthrene. By warming with sodium hyposulphite, a red solution is obtained, colouring unmordanted cotton light-blue in the bath, which changes in the air to flavanthrene yellow.

When flavanthrene is digested for 8 hours with a nitrating mixture, a yellow powder separates, $C_{28}H_8O_{10}N_6$, which appears to be dinitrodinitrosodihydroxyflavanthrene. This is reduced by ammonia and ammonium sulphide to tetra-aminodihydroxyflavanthrene, which, on warming with alkaline hyposulphite, yields a dark-blue vat, dyeing cotton a blue-black, which turns green with hydrochloric acid, owing probably to the formation of a hydrochloride, and again assumes a blue-black colour on washing with water, owing, no doubt, to dissociation (Ber. 1910, 43, 1748).

FLAVASPIDIC ACID *v.* FILIX MAS.

FLAVAURIN. A yellowish-red powder consisting of either the ammonium or sodium salt of dinitrophenolsulphonic acid, and obtained by boiling mononitrophenolortho- or para-sulphonic acid with dilute nitric acid (Leipziger, Anilinfabr. Beyer und Kegel, D. R. P. 27271, June 8, 1883, expired October, 1886). Flavaurin dissolves readily in water, forming a yellow solution, and was introduced as a yellow dye for silk and wool.

FLAVELLAGIC ACID *v.* ELLAGIC ACID.

FLAVENOL *v.* QUINOLINE.

FLAVEOSINE *v.* ACRIDINE DYESTUFFS.

FLAVINE *v.* QUERCITRON BARK.

FLAVOGALLOL. When gallic acid in sulphuric acid solution is treated with arsenic acid and the mixture heated at 110°–120° for 6 hours, a mixture containing flavellagic and coeruleoellagic acids is mainly produced, though when the oxidation is carried out in the presence of 80 p.c. sulphuric acid *flavogallol* $C_{21}H_8O_{12}$ is obtained. This consists of hair-like yellow needles, sparingly soluble in the usual solvents, soluble in sodium hydroxide solution with an orange-yellow colour. With sulphuric acid it yields the *anhydrosulphate* $C_{21}H_6O_{11}\cdot H_2SO_4$, orange-yellow prisms, whereas the *tripotassium* salt $C_{21}H_5O_{12}K_3$, prepared with alcoholic potassium acetate forms an orange-coloured crystalline powder.

Acetylflavogallol $C_{21}H_2O_{12}(C_2H_3O)_6$, small prismatic needles, melts and decomposes at 278°–280°, and the corresponding *benzoyl* compound $C_{21}H_2O_{12}(C_7H_5O)_6$, yellow prisms, at 326°–328°. With boiling aniline flavogallol yields the *anilide* $C_{21}H_7O_{11}\cdot NH\cdot C_6H_5$, which crystallises in yellow needles, melting above 345°. In the paste form flavogallol readily dyes mordanted fabrics, and employing woollen cloth the following shades are produced :—

Chromium.	*Copper.*	*Tin.*	*Iron.*
Dull olive-yellow.	Pale brown.	Pale orange-yellow.	Brownish black.

When acetyl flavogallol is hydrolysed by the acetic ether method, *ethyl flavogallonate* $C_{23}H_{14}O_{13}$, pale yellow needles, is produced, and in a similar manner by the employment of methyl alcohol in this process *methyl flavogallonate* $C_{22}H_{12}O_{13}$ is obtained. By gentle treatment with strong potassium hydroxide solution flavogallol gives *flavogallonic acid* $C_{21}H_{10}O_{13}$, needles, which melt above 300°, and this when acetylated is reconverted into acetyl flavogallol.

The more energetic action of potassium hydroxide solution gives *flavogallone* $C_{20}H_{10}O_{11}$, minute needles, and this yields the acetyl compound $C_{34}H_{24}O_{18}$, leaflets, m.p. 257°–259°.

When flavogallol is methylated with alkali and methyl sulphate and the product is digested with 5 p.c. potassium hydroxide, two apparently isomeric acids $C_{21}H_4O_5(OMe)_{10}$, (*a*) colourless prisms, m.p. 206°–208° and (*b*) m.p. 238°–240°, are obtained, and these both appear to be produced by the addition of three molecules of water to flavogallol and a subsequent methylation of ten hydroxyl groups. These are dicarboxylic acids, and when esterified give the dimethyl ethers of the formula

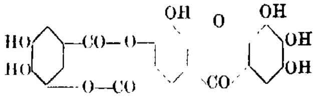
$$C_{29}H_{32}O_{11}(CO_2Me)_2$$

(*a*) melting at 128°–130°, and (*b*) at 86°–87°.

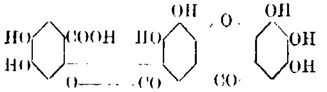
The acid, m.p. 206°–208°, when digested with alcoholic potash at 175° loses one methoxy group with formation of a new acid

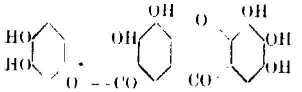
$$C_{28}H_{30}O_{11}(CO_2H)_2$$

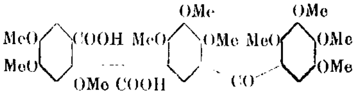
which crystallises in glistening leaflets, m.p. 183°–184°. These reactions suggest the presence in flavogallol of an ellagic acid nucleus, and as a result Bleuler and Perkin (Chem. Soc. Trans. 1916, 109, 543) have tentatively suggested the formula—



for this colouring matter. In case this should prove correct flavogallonic acid (1), flavogallone (2), and the dicarboxylic acid obtained by methylation, m.p. 206°–208° (3), will possess the following constitutions :—

(1)


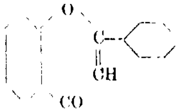
(2)


(3)


A. G. P.

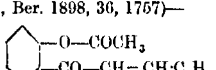
FLAVOLINE *v.* QUINOLINE.

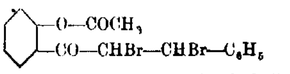
FLAVONE, the mother substance of a large and very important group of natural colouring matters,



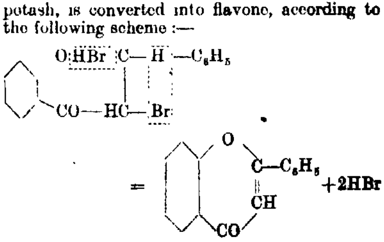
has been synthesised by the following methods :

(*a*) Acetyl-*o*-hydroxybenzylideneacetophenone (1) yields the dibromide (2) (Feuerstein and v. Kostanecki, Ber. 1898, 36, 1757)—

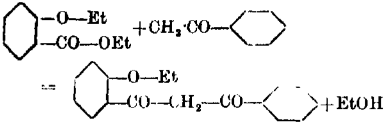
(1)


(2)


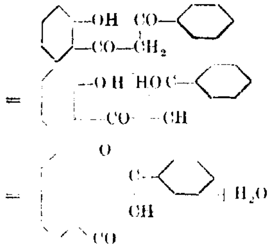
and the latter, on treatment with alcoholic potash, is converted into flavone, according to the following scheme :—



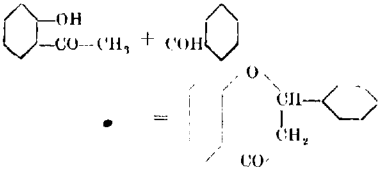
(*b*) Again (v. Kostanecki and Tambor, Ber. 1900, 33, 330), ethyl-*o*-ethoxybenzoate and acetophenone, in the presence of sodium, give *o*-ethoxybenzoylacetophenone—



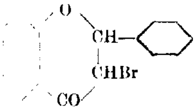
This compound, when digested with boiling hydriodic acid, gives flavone—



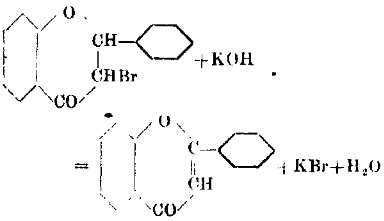
(*c*) Orthohydroxyacetophenone derivatives can be condensed with aromatic aldehydes with production of flavanones (dihydroflavones)—



On treatment with bromine bromflavonone is produced—



and this by means of alkalis splits off hydrobromic acid and is converted into the flavone—

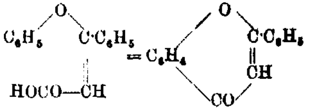


(v. Kostanecki, Levi, and Tambor, Ber. 1899 32, 326).

(*d*) Ruhemann (Ber. 1913, 36, 2188) has employed for the synthesis of flavone the esters of β-hydroxyaryl cinnamic acids. These may be prepared by the interaction of phenyl propiolic acid esters with sodium phenolates—

$$C_6H_5·C:C·COOEt+NaO·C_6H_5$$
$$=C_6H_5·C(OC_6H_5):CNa·COOEt$$

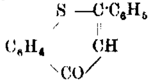
These esters are readily transformed into the free acids, the chlorides of which by means of aluminium chloride give the corresponding flavones. Thus β-phenoxy cinnamic acid in this way gives flavone—



and substituted flavones can be readily prepared by the employment of cinnamic acids containing other hydroxyaryl nuclei. Phenyl thiocinnamic acid from thiophenol and phenyl propiolic acid ethyl ester

$$C_6H_5·C(SC_6H_5):CH·COOH$$

in this manner yields *thioflavone*—

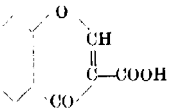


a compound which crystallises in yellow needles and closely resembles flavone.

In case the β-hydroxyaryl cinnamic acids are here replaced by the corresponding derivatives of fumaric acid, benzo-γ-pyrone (*chromone*), carboxylic acids are produced which readily evolve carbonic acid gas with formation of chromone. Thus β-phenoxy-fumaric acid

$$COOH·C(OC_6H_5):CH·COOH$$

gives benzo-γ-pyrone (chromone) carboxylic acid [1]—



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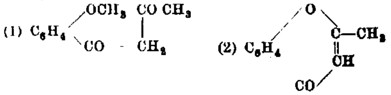
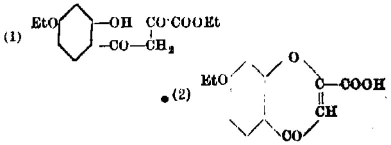
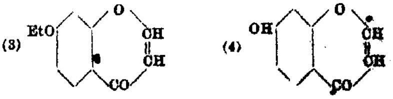
[1] Though chromone itself was first obtained by Ruhemann and Stapleton (*loc. cit.*), chromone derivatives had been prepared slightly earlier by v. Kostanecki (Ber. 1900, 1998), who employed for this purpose methods similar to those he had found serviceable for the synthesis of flavone compounds. Thus the diketone (1), (compare method (*c*) above) obtained by the interaction of *o*-methoxy-benzoic acid methyl ester, and acetone on treatment with hydriodic acid, gives β-methyl-chromone (2)—



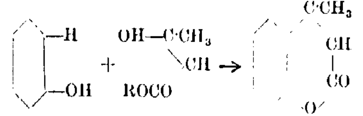
Again, according to v. Kostanecki, Paul, and Tambor, the diketone (1) prepared from resacetophenone mono-ethyl ether and ethyl oxalate, on treatment with alcoholic hydrochloric acid gives 3 ethoxychromone carboxylic acid (2)—



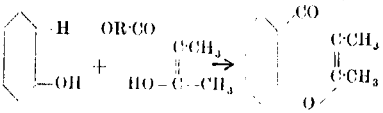
This when melted gives 3 ethoxychromone (3), and by means of hydriodic acid can be converted into 3 hydroxychromone (4)—



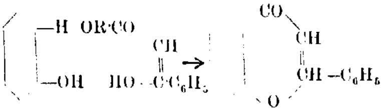
(*e*) Simonis (Ber. 1914, 47, 2229), again, has described another method for the synthesis of flavone. Whereas Pechmann and Duisberg found that phenols could be condensed by means of sulphuric acid with the esters of β-ketonic acids, to form α-pyrone (coumarin) derivatives, according to the following equation which illustrates the preparation of methyl-coumarin from phenol and acetoacetic ether,



by employing phosphorus pentoxide as the condensing agent the reaction takes another course. Thus phenol and methylaceto-acetic ether in this way gives dimethyl-chromone (Petschek and Simonis, Ber. 1913, 46, 2014)—



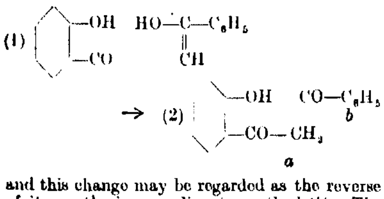
whereas benzoyl-acetic ether and phenol (*ibid.* 1914, 46, 2232) give flavone



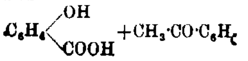
For the preparation of chloroflavones, *see* Ruhemann (Ber. 1921, 54, 912), and aminoflavones, *see* Bogert and Marcus (J. Amer. Chem. Soc. 1919, 41, 83). *Flavone* crystallises from ligroin in colourless needles, m.p. 97°, and is readily soluble in the usual organic solvents. Its solution in sulphuric acid is yellow and possesses a weak blue fluorescence.

By the action of alkalis, flavone and hydroxyflavones suffer hydrolysis according to the following scheme:—

The first product of the reaction owing to the disruption of the pyrone ring is the β-diketone (2)—

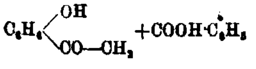


and this change may be regarded as the reverse of its synthesis according to method (*b*). The ketone then suffers further hydrolysis as shown by the dotted lines (*a*) into acetophenone and salicylic acid—



$$C_6H_4\left\langle\begin{matrix}OH\\COOH\end{matrix}\right. + CH_3{\cdot}CO{\cdot}C_6H_5$$

or (*b*) *o*-hydroxy acetophenone and benzoic acid—

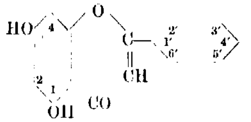


$$C_6H_4\left\langle\begin{matrix}OH\\CO{-}CH_3\end{matrix}\right. + COOH{\cdot}C_6H_5$$

The products of the hydrolysis of naturally occurring flavone colouring matters have in the past been mainly instrumental in determining their constitution.

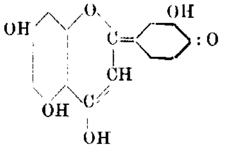
All natural hydroxyflavones which have at present been carefully examined dye aluminium mordanted fabrics a yellow shade, the intensity of which is dependent upon the position of their hydroxyl groups.

Thus chrysin-1 : 3-dihydroxyflavone

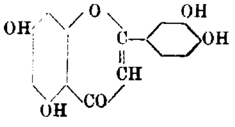


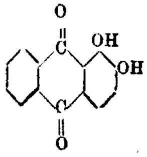
and apigenin-1 : 3 : 4′-trihydroxy flavone possess but feeble dyeing property,[1] whereas luteolin-1 : 3 : 3′ : 4′-tetrahydroxy flavone is a strong colouring matter. Though Liebermann and v. Kostanecki's rule is in this instance but partially applicable, it is evident that the dyeing property in the flavone group is only fully developed when at least two hydroxyls in the ortho- position to one another are present. There is every reason to anticipate also that a 3 : 4-dihydroxy-flavone would, like luteolin, possess well-marked dyeing properties. Of the influence, however, of such a grouping in the positions 2′ : 3′ : 2 : 3 and 1 : 2, information is at present lacking, as compounds possessing these characteristics have as yet to be discovered.

According to the quinonoid theory, it has been suggested that the flavone colouring matters, at least in the form of their lakes, may possess a paraquinonoid structure, which in the case of luteolin may be represented thus—



and such a formula has been applied by Perkin (Chem. Soc. Trans. 75, 433) to the monoalkali and oxonium salts of these compounds. It has been pointed out by Watson (Chem. Soc. Trans. 1914, 105, 759) that dyes which are quinonoid in all possible tautomeric forms exhibit a deep colour, the opposite being generally the case with those which cannot be represented in this way. Numerous instances are cited to illustrate this point, for which the paper itself should be consulted, but an examination of the formula of luteolin and alizarin will render sufficiently clear the theory of this author—





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[1] The shades given by these and other feeble colouring matters of a similar type can be more satisfactorily observed by employing mordanted wool rather than mordanted calico.

Luteolin, the only flavone colouring matter possessing strong dyeing property which has been carefully examined, gives shades possessing considerable fastness to light, and these are much more permanent than those given by the present known members of the flavonol group.

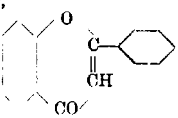
NATURAL FLAVONE.

Very interesting is the occurrence of flavone in nature (Müller, Chem. Soc. Trans. 1915, 107, 872). It is well known that many varieties of the primula possess on their flower stalks, leaves, and seed capsules a characteristic dust termed by gardeners 'meal' or 'farina,' and this is most pronounced on varieties obtained from China and Japan. This powder, examined by Hugo Müller who obtained it mainly from the *P. pulverulenta* and *P. japonica*, dissolves readily in benzene and boiling ligroin, and the concentrated solution on cooling became semi-solid owing to the separation of crystalline tufts.

It possessed the formula $C_{15}H_{10}O_2$, melted at 99°–100°, and on boiling with dilute sodium hydroxide gave slowly a yellow solution, with formation of a small quantity of acetophenone, and the latter could be obtained in greater quantity by the action of methyl alcoholic sodium hydroxide. Employing methyl alcoholic barium hydroxide, a reagent not previously suggested for the degradation of flavone compounds, Müller obtained a substance $C_{15}H_{12}O_3$. This by the action of alkalis was converted into salicylic acid and acetophenone and evidently consisted of hydroxy-benzoyl-acetophenone (*o*-hydroxy-dibenzoyl-methane)—

$$OH\cdot C_6H_4\cdot CO\cdot CH_2\cdot CO\cdot C_6H_5$$

The compound $C_{15}H_{10}O_2$ was thus without doubt *flavone*,

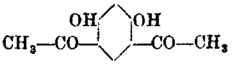


and it is interesting to note that though hydroxy-benzoyl-acetophenone was assumed by Feuerstein and v. Kostanecki (Ber. 1898, 31, 1758) to be the first product of the hydrolysis of this substance, its isolation in this manner had not previously been effected.

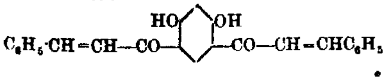
The function which flavone exercises in the economy of the plant life of the primula is difficult to explain, though it may be of service on account of its repellent action towards water.

DIFLAVONE.

This substance was prepared by Ryan and O'Neill (Proceedings Royal Irish Academy, xxxii. B, 5, 48), who employed as a starting-point for their synthesis diacetoresorcinol—



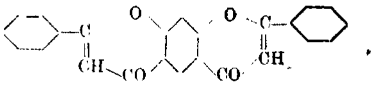
This by interaction with benzaldehyde yields the dichalkone



the acetyl compound of which when brominated forms the tetrabromide

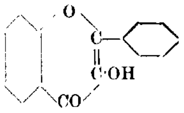
$$C_6H_5(O\cdot COCH_3)_2(CO\cdot CHBr\cdot CH\cdot Br\cdot C_6H_5)_2$$

Alcoholic potash converts the latter compound into *diflavone*—



and this crystallises in faint yellow needles, m.p. 277°–278°. In its general properties diflavone resembles flavone, and its faint yellow solution in sulphuric acid has a beautiful blue fluorescence. Colouring matters of this group are at present unknown. A. G. P.

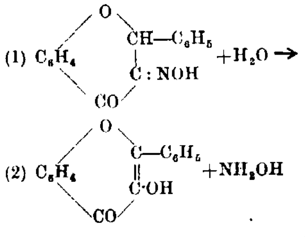
FLAVONOL



It is usual to subdivide the great family of yellow colours derived from flavone into two classes, *flavone* and *flavonol*, and the latter group is distinguished by the fact that the hydrogen in the γ-pyrone ring of these compounds is substituted by hydroxyl, whereas in the former it is not.

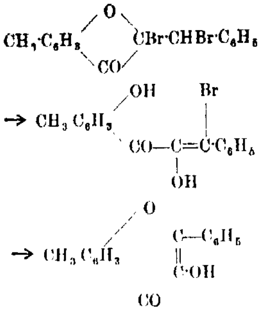
Flavonol, so designated by v. Kostanecki, was synthesised by v. Kostanecki and Szabránski (Ber. 1904, 37, 2819) in the following manner:—

By the action of amyl nitrite and hydrochloric acid in alcoholic solution on flavanone, *iso*nitrosoflavanone (1), m.p. 158°–159°, is produced, and this by means of boiling dilute acids splits off hydroxylamine and is converted into flavonol—

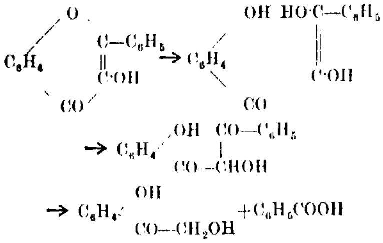


Flavonol crystallises from alcohol in yellow needles, m.p. 169°–170°. When warmed with aqueous sodium hydroxide it forms a yellow liquid, and on cooling the sodium salt separates in the form of yellow needles. Its solution in sulphuric acid exhibits an intense violet fluorescence. *Acetylflavonol*, colourless needles, melts at 110°–111°.

According to Auwers and Müller (Ber. 1908, 41, 4233), benzylidenecoumaranones can be converted into flavonols. Thus benzylidene-4-methylcoumaranone dibromide when treated with potassium hydroxide gives 2-methylflavonol. The reaction may be thus expressed:—



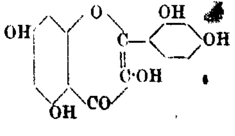
The hydrolysis of flavonol into *o* hydroxybenzoylcarbinol and benzoic acid may be expressed by the following equations :—



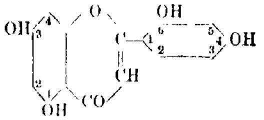
and this reaction, which is typical of the behaviour in these circumstances of the whole series of these compounds, has in general been employed to ascertain their structure. It is best effected by digesting the fully methylated flavonols with boiling alcoholic potash for some hours, for owing to the occurrence of secondary reactions it cannot be satisfactorily carried out with the unmethylated compounds.

For the synthesis of numerous flavonols, many of which occur naturally, v. Kostanecki and his co-workers have employed as a general method that found serviceable for the preparation of flavonol itself. The flavonols, with the exception of morin, which curiously enough is colourless, are yellow crystalline substances, soluble in alkaline solutions with a yellow colour, and yield with ease in the presence of acetic acid orange crystalline oxonium salts. According to Perkin, whereas as a rule hydroxyflavones are not oxidised by air in alkaline solution and can be precipitated therefrom unchanged by acids, flavonols, on the other hand, are readily decomposed in this manner with the formation of water-soluble products.

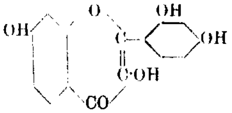
Interesting is the fact that though certain colouring matters of this group do not possess two hydroxyls in the ortho- position relatively to one another, they are nevertheless strong dyestuffs, and of these the tetrahydroxyflavonol morin may be taken as an example—



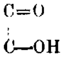
That this peculiarity arises from the presence of the pyrone hydroxyl is evident if the structure of morin is compared with the lotoflavone of Dunstan and Henry (Phil. Trans. 1901, 194, 515)



the tinctorial properties of which are exceedingly feeble. It seemed possible that this dyeing effect was to be attributed to the fact that this compound contains the hydroxyl (1) in the peri-position to the chromophore and which is present in most of the natural dyes of this group. Such a suggestion, however, became untenable on the synthesis of resomorin—



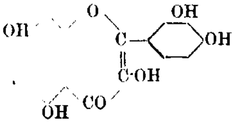
by Bonifazi, v. Kostanecki, and Tambor (Ber. 1906, 39, 86), which dyes the same shades as morin but does not contain the peri-hydroxyl in question. Evidently therefore the tinctorial properties of these hydroxy flavonols can only be accounted for by their possession of the grouping



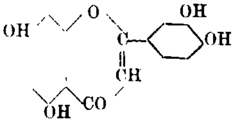
$$\begin{array}{l} C=O \\ \vdots \\ C-OH \end{array}$$

the effect of which is considerably strengthened by the presence of hydroxyls in other positions in the molecule, and this has received support from the observation of v. Kostanecki and Szabránski that flavonol itself dyes on aluminium mordant a pale yellow shade. Though ortho-hydroxyl groups are not essential to the dyeing property of hydroxyflavonols, their presence, at least in certain positions, has considerable influence, not only in deepening the tone, but also in reddening the shade. Thus, whereas morin dyes bright yellow shades, quercetin (1)

(1)



(2)



gives a brown-orange shade on aluminium mordant, and the effect of the pyrone hydroxyl is very evident on comparing quercetin with luteolin (2) which gives in the same way only a bright yellow colour. A multiplication of hydroxyls does not effect any general alteration of shade given by these compounds, as is so well known to take place in the anthraquinone group.

The shades given by the flavonols are not so fast to light as those given by the flavone luteolin, and this may arise in part owing to the greater susceptibility of their salts (or lakes) to oxidation. In this respect they vary again among themselves, quercetin being a somewhat faster colour than fisetin, and morin than quercetin.

On the other hand, the character of the shade given by the natural dyestuff varies in tone, as to whether the colouring matter is present as glucoside or in the free condition. Thus in dyeing with quercitron bark, quercitrin and not quercetin is the dyestuff, whereas in old fustic no glucoside is present, and the tinctorial effect is due to morin itself. The shade again given by a glucoside is naturally dependent on the position of the sugar nucleus, and thus the quercetin glucoside, quercimeritrin (*see* Cotton Flowers) has quite distinct properties in this respect from quercitrin itself. Again, a glucoside may be almost devoid of tinctorial property, as in the case of the kaempferol glucoside robinin and the alizarin glucoside ruberythric acid. The idea formerly held that glucosides in general were not true dyestuffs, and that during the dyeing operation by the action of the mordant they were hydrolysed with production of the colour lake of the free colouring matter, is incorrect. This evidently arose from the fact that in certain of these dyestuffs, as, for instance, madder and Persian berries, the glucoside is accompanied by its specific enzyme, which in case the temperature of the dye-bath is gradually raised from the cold upwards, effects the hydrolysis of the glucoside before the dyeing operation has really commenced. A. G. P.

FLAVOPURPURIN *v.* ALIZARIN AND ALLIED COLOURING MATTERS.

FLAX. This term, as applied to the fibre of commerce, designates the product of the plant *Linum usitatissimum* (Linn.), belonging to the nat. order *Linaceæ*, a group consisting of herbs and small shrubs indigenous to all temperate climates. *Linum usitatissimum* is now only found in its cultivated condition. The plant occurs in two main 'forms': *L. usitatissimum f. vulgare* or *indehiscens*, with a taller stem and fruits that do not split open spontaneously; and *L. usitatissimum f. humile* or *crepitans*, more richly flowered and with fruits that open spontaneously. The former form is cultivated for the production of fibre, the latter for the production of seed (linseed). The herb has a solitary erect stem, attaining a height of from 20 to 40 inches. The cultivation of flax is of insignificant extent in England and Scotland, but is of much greater importance in Ireland. It forms also an important crop in some parts of Belgium, Holland, France, and Russia.

The plant having attained about two-thirds of its full height, is ready for gathering; as when allowed to grow to maturity a coarser and less valuable fibre results. The stem consists of an internal woody core, an external cortex, and an intermediate cellular tissue (the bast), from which the flax is prepared. The operations necessary in the preparation of the fibre for the purposes of the spinner are (1) pulling; (2) rippling; (3) steeping, retting, or watering; (4) grassing; (5) breaking; (6) scutching; (7) heckling. Of these, 'pulling' is a distinctive method of gathering the flax plant, which is always torn up by the roots and not cut down like other crops. A fine day is selected for this purpose, and the stems are as far as possible arranged in sizes by the pullers; those also being assorted which may have been damaged by wind and rain. 'Rippling' is the process of removing the seed balls by drawing the heads through a species of comb set up usually in the field wherein the flax is being harvested. 'Retting' consists in immersing the stems in pools or streams of water in such a position that they shall stand almost erect, although weighted down so as to be quite submerged. The object of this is to induce fermentation, which dissolves the glutinous matter and disintegrates the fibres. Pure soft water and great judgment in the proper length of time to be allowed, which may be ten days to a fortnight, are essentials in this part of the treatment. Retting is followed by 'grassing,' whereby the separation of the flax fibre from the ligneous portions of the stalk is further facilitated. It consists in spreading the stems on the grass, for a week or a fortnight, during which time they are occasionally turned. The flax during this operation becomes somewhat bleached. 'Breaking' and 'scutching' are the means employed to strip off the hard epidermis, and are effected either by hand or machinery. 'Heckling' is a still further combing, which arranges the fibres in parallel order, ready for the manufacture of yarn.

According to Kolb, retting sets up a peculiar fermentation, which results in pectose or its analogous bodies being changed into pectin and pectic acid; of which the former being soluble is left in the water, whilst the latter being insoluble remains attached to the fibre until its treatment with hot alkaline lye in bleaching, when it is changed into soluble metapectic acid.

Under the microscope, flax fibre has the appearance of a cylindrical tube, not continuous as in the case of cotton, but broken up by septa or knots at irregular distances through the length of the fibre, varying from four to six times the diameter of the tube. This diameter is from about $\frac{1}{1100}$ to $\frac{1}{1800}$ of an inch. The adhesive power of the fibres, which gives the strength when spun into yarn, appears to depend on the twist given by the spindle as well as by the tenacity of the rough cellular sheath, which remains always more or less incrusted with the characteristic resinous deposit. Advantage is taken of the presence of this gummy deposit to detect the admixture in fabrics of cotton with linen; as, although the ultimate basis of both is cellulose, cotton exists in a much purer state than flax. The difference in the reaction upon them by caustic alkalis points out such admixture. When immersed in a boiling solution of caustic potash and water for about a minute, and then pressed between folds of filter paper, flax exhibits a dark-yellow colour, whilst cotton, when similarly treated, either remains white or becomes a very bright yellow. The same solution of potash employed cold colours raw flax orange-yellow, whilst cotton becomes grey, a result which Kuhlmann believed to be due to the pectic substances contained in flax.

FLEMINGIN *v.* WARAS; RESINS.

FLINT. (Fr. *Silex*; Ger. *Feuerstein.*) A native form of silica, being a compact massive variety of the mineral quartz with some admixed hydrated silica (opal). It grades into chalcedony, chert, hornstone, or jasper, and may be banded and marked like agate; no sharp line of demarcation can be drawn between these several varieties of quartz. The term 'flint' is commonly limited to the nodular masses found in, or derived from, the Chalk formation. This material is of organic origin, being derived from the siliceous (opaline) remains of marine organisms (sponges with siliceous spicules, radiolaria, and diatomaceæ) deposited on the sea-floor together with the calcareous remains of other organisms which gave rise to the chalk itself. After deposition, this disseminated siliceous material became segregated into nodules; being no doubt re-deposited in the colloidal condition, and subsequently dehydrated and transformed into the crystalline condition. The fact that nodules of flint are usually arranged along the bedding planes in the chalk would suggest that these layers correspond to periods when siliceous organisms predominated, and that the solution and re-deposition of the silica took place contemporaneously in the soft ooze. On the other hand, the occurrence of flint in platy forms filling vertical joints in the chalk, suggests that solution and re-deposition may also have taken place subsequent to the consolidation of the chalk.

Flint is dull in colour and lustre, being yellowish, blackish, or more usually of a smoke-grey colour, and with a more or less waxy or greasy appearance. It breaks with a smooth conchoidal fracture, and under certain conditions with a conical fracture. Thin flakes are translucent at the edges. Thin sections in polarized light show that a large part of the material is minutely crystalline (crypto-crystalline). Sp.gr. 2·60–2·63 (somewhat less than that of crystallised quartz). The material consists of nearly pure silica (about 98 p.c.) with 1–1·4 p.c. of water, and traces of iron, aluminium, calcium, and organic matter. It is much more readily soluble in a hot solution of caustic alkali than is crystallised quartz. The white patina or crust often seen on flints consists in some cases of adhering chalk mixed with silica ($CaCO_3$ 50 p.c.); or more often it consists wholly of silica, and has been produced by the weathering of the material, the opal being dehydrated or removed in solution and the crystalline particles liberated in a powdery condition.

Flints occur principally in the Upper Chalk, which is of wide distribution in the south-east of England, around the Paris basin, in Denmark, the island of Rügen, Co. Antrim, &c. With the denudation of the rock the resistant flints accumulate in gravels and other secondary deposits. The material is obtained: (1) as irregular nodules coated with chalk as a by-product from chalk quarries worked for lime, cement, whitning, &c.; (2) iron-stained pebbles from gravel pits; (3) boulders and pebbles collected on the seashore.

Flint was perhaps the very first mineral to be worked for practical uses, as witness the prehistoric palæolithic implements and the highly finished flints of the neolithic period. Flints for tinder-boxes and gun-flints are still worked by the flint-knappers at Brandon, in Suffolk (for an account of this industry, v. S. B. J. Skertchly, Mem. Geol. Survey, 1879). Apart from the local use of flint as a building stone (*v.* E. T. Baggallay, Trans. R. I. Brit. Arch. 1885), and for road making and concrete, the principal use of the material is in the ceramic industry. For this purpose large quantities are collected along the French coast between Havre and St. Valery at the mouth of the Somme. The material is burnt and thrown into cold water, when it can readily be finely ground to a snow-white powder; large quantities of flint pebbles are also ground between blocks of chert. For the manufacture of porcelain, as well as for glazing and enamelling, powdered flint is better than crystallised quartz, probably on account of the difference in texture of the material. Formerly it was also used in the manufacture of glass (hence the term flint-glass). Powdered flint bonded with a highly plastic clay is used for making refractory silica-bricks for steel furnaces. Round nodules of flint are used in tube mills for grinding felspar, cement-clinkers, ore, &c., the silica worn from them being an uninjurious contamination. The Danish flints are best suited for this purpose. As an inert material it is used as a filler in acid towers. Powdered flint is used for making sand-paper. Flint is also cut and polished for use as agate-mortars, polishers, and burnishers. (*v.* W. Hill, Flint and Chert, Proc. Geol. Assoc. 1911, xxii. 61; J. W. Mellor and A. J. Campbell, Flint and Quartz, Trans. English Ceramic Soc. 1916, xv. 76). L. J. S.

FLORENCITE. Basic phosphate of aluminium and cerium (Ce_2O_3, &c., 28 p.c.)—

$$AlPO_4{\cdot}CePO_4{\cdot}Al(OH)_6,$$

crystallised in the rhombohedral system and isomorphous with the strontium salt hamlinite. Sp.gr. 3·586. It is found as small yellowish grains and crystals in diamond-bearing sands near Diamantina, Brazil, and in cinnabar-bearing sands and in mica-schist with topaz near Ouro Preto, Brazil. L. J. S.

FLORES CINAE *v.* SANTONICA.

FLORIDOSE. An aldohexose found in the red sea-weed, *Florideæ*, and in *Chondrus Elatus*, *Ahnfeltia pricata*, and other sea plants. Crystallises from water; is soluble in alcohol; m.p. 152°–153°; $[\alpha]_D^{20}+80{\cdot}75°$. Reduces Barreswil's (Fehling's) solution; is fermented by yeast; forms a hydrazone, m.p. 158°–160°. Soluble in methyl and ethyl alcohols and in hot water; a needle-shaped osazone, m.p. 193°. Sodium amalgam reduces it to a hexahydric alcohol, *floriditol* (Takahashi, J. Tokyo Chem. Soc. 1919, 40, 157).

FLOS-FERRI *v.* ARAGONITE.

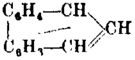
FLUID GELATIN *v.* *Aluminium oleate*, art. ALUMS.

FLUOCERITE. Fluoride of cerium (40 p.c.), lanthanum (30 p.c.), and yttrium (3 p.c.) earths, (Ce, La, Di) F_3, crystallised in the hexagonal system. It is reddish-yellow with resinous lustre, and massive, rarely as crystals. Sp.gr. 5·70, 5·93. It occurs in pegmatite veins with gadolinite, orthite, &c., at Österby, Finbo, and Broddbo in Sweden (P. Geijer, Geol. För Förh. Stockholm, 1921, 43, 19). L. J. S.

FLUORAL *v.* SYNTHETIC DRUGS.

FLUORAM. Trade name for acid ammonium fluoride.

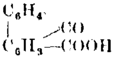
FLUORANTHENE *Idryl*



$$\begin{array}{l} C_6H_4\text{—}CH\diagdown \\ |\qquad\qquad\quad >CH \\ C_6H_3\text{—}CH\diagup \end{array}$$

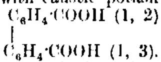
Discovered independently by Fittig and Gebhard (Ber. 10, 2143; Annalen, 193, 142) in coal tar and by Goldschmiedt in 'stupp,' a mixture of hydrocarbons obtained in distilling mercury ores at Idria (Ber. 10, 2022). Obtained from the fraction of coal tar boiling higher than anthracene, by redistilling it at 250° under a pressure of 60 mm. A mixture of pyrene and fluoranthene passes over, which may be separated by repeated crystallisations from alcohol of their picric acid compounds; the fluoranthene picrate separates as long reddish-yellow needles, melting at 182°–183°. Forms slender needles or monoclinic plates, melting at 109°–110°; boils at 250°–251° under a pressure of 60 mm. Sparingly soluble in cold, readily soluble in boiling alcohol; soluble in ether, carbon disulphide, chloroform, benzene, and glacial acetic acid. Warm concentrated sulphuric acid dissolves the hydrocarbon, producing a deep-blue colour.

Chromic acid oxidises it to a quinone $C_{15}H_8O_2$ (red needles melting at 187°–188°), which, on further oxidation, yields *diphenyleneketone-carboxylic acid*



$$\begin{array}{l} C_6H_4\diagdown \\ |\qquad\quad CO \\ C_6H_3\text{—}COOH \end{array}$$

(m.p. 191°–192°). This acid is converted by heating with lime into *diphenyleneketone* (*v.* FLUORENE), and by fusion with caustic potash into *isodiphenic acid*

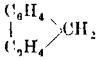


$$\begin{array}{l} C_6H_4{\cdot}COOH\ (1,\ 2) \\ | \\ C_6H_4{\cdot}COOH\ (1,\ 3). \end{array}$$

Fuming nitric acid forms with the hydrocarbon a trinitro derivative.

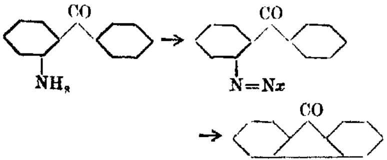
FLUOR-APATITE *v.* APATITE.

FLUORENE *o-Diphenylene methane*

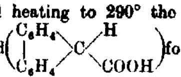


$$\begin{array}{l} C_6H_4\diagdown \\ |\qquad\quad >CH_2 \\ C_6H_4\diagup \end{array}$$

Discovered by Berthelot in coal tar (Compt. rend. 65, 465; Ann. Chim. Phys. [4] 12, 222). Obtained (1) by passing the vapour of diphenylmethane through a red-hot tube (Gräbe, Annalen, 174, 194); (2) by reduction of diphenylene ketone either by distillation with zinc-dust (Fittig, Ber. 6, 187) or by heating with hydriodic acid and red phosphorus to 150°–160° (Gräbe, *ibid.* 7, 1625): the diphenylene ketone may be synthesised by splitting off H_2O and CO_2 from diphenic acid (Ostermayer and Fittig, *ibid.* 5, 935) or by diazotising *o*-amino-benzophenone and eliminating the diazo- group (Gräbe and Ullmann, *ibid.* 27, 3485)



(3) by condensing ethyl trichloracetate with benzene in the presence of aluminium chloride and heating to 290° the 9-fluorene carboxylic acid



$$\left(\begin{array}{l} C_6H_4\diagdown\quad\diagup H \\ |\qquad\quad C \\ C_6H_4\diagup\quad\diagdown COOH \end{array}\right)$$

formed (Delacre, Bull. Soc. chim. [3] 27, 875). The high-boiling fractions of tar oil after depositing naphthalene and anthracene are distilled; the fraction boiling between 295° and 310° contains the greater portion of the fluorene, which, on fusion with caustic potash at 280°, is converted into a solid potassium compound (Weissgerber, Ber. 34, 1659): the latter was originally separated mechanically from the fused hydrocarbons and the fluorene regenerated by treatment with water (D. R. P. 124150). Diphenylene oxide, present in the original mixture, is converted into potassium diphenate, and a small proportion of fluorene into *o*-phenylbenzoic acid; the alkaline mass is then treated with water and the hydrocarbons obtained pure by fractional distillation (D. R. P. 130679). The sodium compound, also used for the separation, is obtained by fusing the mixture of hydrocarbons with sodium or sodamide at 150°–200° (D. R. P. 203312). In the presence of aniline or other organic bases, the reaction proceeds more smoothly, and at a lower temperature (D. R. P. 209432). Recrystallisation from alcohol and glacial acetic acid, and precipitation of the picric acid compound (m.p. 81°), may be used in the purification.—Lustrous laminæ, melting at 115° (Delacre, *l.c.*). Boils at 294°–295° (corr.). Sparingly soluble in cold, readily in hot alcohol; readily soluble in ether, benzene, and carbon disulphide. Oxidation with lead oxide yields bisdiphenylene ethane and bisdiphenylene ethylene (red needles melting at 188°); with chromic acid diphenyleneketone (yellow prisms melting at 84°, boiling at 337°); with fused caustic potash *o*-phenylbenzoic acid and with potassium permanganate *o*-phthalic acid. With nitric acid (sp.gr. 1·4) in glacial acetic solution at 80°, 2-nitrofluorene is formed (Diels, Ber. 34, 1758); fuming nitric acid produces the 2 : 7-paradinitro derivative, melting at 199°–201° (Fittig and Schmitz, Annalen, 193, 134), 255°–260° (Barth and Goldschmiedt, Ber. 11, 846). The corresponding amino compounds have been used in the preparation of azo dyes, but do not yet appear to have found practical application. By the action of sulphuric acid and the halogens, substitution compounds are formed. The negative character of the methylene hydrogen atoms is shown by the formation of potassium and sodium compounds (*v. supra*), and by the formation of condensation products with benzaldehyde and oxalic ester (Thiele, Ber. 33, 851; Wislicenus, *ibid.* 33, 771). The conversion of phenanthrenequinone, by fusion with potash, to 9-oxyfluorene-9-carboxylic acid (Schmidt and Bauer, Ber. 38, 3738), and the formation of phenanthrene by a pyrogenic reaction from methyl fluorene (Gräbe, *ibid.* 37, 4145), furnish instances of the mutual conversion of 5 and 6 rings. Reduction with hydriodic acid yields a decahydrofluorene, $C_{13}H_{20}$ (Schmidt, *ibid.* 40, 4566); fluorene perhydride $C_{13}H_{22}$, is described by Spiegel (*ibid.* 41, 884; 42, 916).

Isomeric diphenylenemethanes were described by Carnelley (Chem. Soc. Trans. 1880, 708), who obtained them by passing the mixed vapours of benzene and toluene through a red-hot tube. I. S.

FLUORENE KETONE *v.* KETONES.

FLUORESCEÏN *v* TRIPHENYL METHANE COLOURING MATTERS.

FLUORESCENT BLUE or **RESORCIN BLUE** $C_{18}H_8Br_6N_2O_5(NH_4)$. A colouring matter obtained in 1880 by Weselsky and Benedikt by treating a solution of diazoresorufin in potassium carbonate with bromine, and precipitating with an acid. Soluble in boiling water, giving a reddish-violet solution with green fluorescence. On the addition of hydrochloric acid, the aqueous solution gives a yellowish-brown precipitate. With zinc-dust and caustic soda solution rapidly becomes colourless, but again becomes blue on exposure to air Soluble in concentrated sulphuric acid with blue colour, which becomes violet on addition of water, and eventually gives a reddish-brown precipitate Dyes silk and wool blue with brownish fluorescence (Brünner and Krämer, Ber 17, 1847, 1867, 1875; Weselsky and Benedikt, Monatsh. 5, 605; Ber. 18, Ref. 76) (*v.* OXAZINE COLOURING MATTERS).

FLUORINDINES *v.* AZINES.

FLUORINE. Sym. F. At. wt. 19·0. Ampère, in 1810, first pointed out the analogy between hydrochloric acid and the gas evolved from a mixture of fluorspar and sulphuric acid; he assumed the existence of an element similar to chlorine, and further that the acid obtained from fluorspar was a hydrogen compound. Berzelius and Davy, a few years later, more fully established this view.

The name fluorine was given to the supposed element on account of its being a constituent of fluorspar. Many fruitless attempts had been made to isolate the element, but, owing to its great affinity for other elements, none could be regarded as successful until Moissan, in 1886, announced his results.

Occurrence.—Fluorine occurs in the combined state only, and generally as fluor-spar CaF_2, crystallising in cubes and octahedrons; this compound is found in abundance in Derbyshire, where it is known as Derbyshire-spar, and 'Blue John'; it is also found in Northumberland, Durham, Yorkshire, and Cornwall, and from it most of the preparations of fluorine are made (*v.* FLUOR-SPAR). *Cryolite*, a double fluoride of aluminium and sodium $3NaF{\cdot}AlF_3$ or $Al_2F_6{\cdot}6NaF$, found in Greenland, is a mineral containing fluorine (*v.* CRYOLITE). Fluorine is widely but sparingly diffused, occurring in small amount in conjunction with aluminium and silicon in *topaz*; with cerium and yttrium in *fluocerite* and *yttrocerite*; it occurs also in *apatite*, *wavellite*, *wagnerite*, and other minerals. It is also found in the *idocrase* of Vesuvius, Christiansand in Norway, and in the variety from the River Wilui in Siberia (Jannasch, Jahr. Mineral. 1883, 2, 123). Traces of it exist in sea-water, and in the water of many mineral springs and rivers. Traces of fluorine have been detected by Wilson in the silicious stems of grasses and equisetaceous plants. Bones, both fossil and recent, contain fluorine (Carnot, Compt. rend. 1892, 114, 1189–1192), and it is found in the enamel of the teeth (Gabriel, Zeitsch. physiol. Chem. 18, 257–303, 1894; Wrampelmeyer, Zeitsch. anal. Chem. 32, 550–553, 1894). It is said to occur in the blood, the brain (Horsford, Annalen, 149, 202), and in milk, also in human urine.

Tammann (Zeitsch. physiol. Chem. 1888, 12, 322–326) has shown that fluorine is of great importance in the animal economy, while Saber Horstmann (Ann. Chim. Phys. 114, 510) has demonstrated that certain plants do not develop in its absence.

Isolation of fluorine.—Davy concluded, from his experiments on the compounds of fluorine, that the latter was an extremely active element. Since his time many chemists have endeavoured to obtain fluorine in the free state. It has been known since the time of Faraday that strong hydrofluoric acid is a very bad conductor of the electric current, and Moissan in his experiments found that the current from 50 Bunsen cells was not able to effect a passage through the anhydrous acid; by dissolving a little hydrogen potassium fluoride $HF{\cdot}KF$ in the acid, it was at once rendered a conductor The apparatus employed consisted of an irido-platinum U-tube 9·5 cm. high and 1·5 cm. diameter (Fig. 1). At the side and near the top of each limb was a small exit tube of platinum, F and H; each limb of the U-tube was provided with a hollow cylinder screwed into it, and the hollow part of each cylinder was closed by a stopper of fluorspar, through the axis of which passed the terminals of iridio platinum (Fig. 2); these terminals were 2 mm. square in section and side, 12 mm. long, and passed to within 3 mm. from the bottom of each limb. The whole apparatus was first entirely freed from moisture by drying at 120°, then about 6 grams of the double fluoride of hydrogen and potassium were introduced, the stoppers screwed in and covered with shellac, and then placed in a methyl chloride bath, a constant supply of which at −23° was maintained in the bath. The delivery tubes, hitherto kept in communication with desiccators of fused potash, are now connected with the vessel containing anhydrous hydrofluoric acid, and about 16 grams are gently aspirated into the apparatus. On now passing a current from 20 Bunsen cells through the solution, a continuous evolution of gas took place. To demonstrate its effects upon other bodies, they were placed in small glass tubes, and brought to the delivery tube at the positive side (Fig. 3).

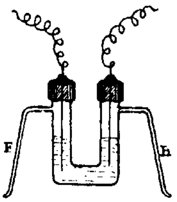


FIG. 1.

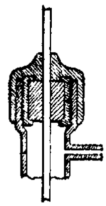


FIG. 2.

On taking the apparatus to pieces after each experiment, the hydrofluoric acid remaining was found to contain a small quantity of platinum fluoride in solution, and a black mud consisting of a mixture of iridium and platinum in suspension. The negative electrode was not attacked, but the platinum rod forming the positive pole was eaten away to a point, so that one rod only served for two experiments. The average delivery of gas was about 1·5 to 2 litres per hour.

It is probable that potassium fluoride is first decomposed, fluorine being evolved at the positive pole, and potassium, which decomposes hydrofluoric acid, liberating its equivalent of hydrogen at the negative pole, re-forming potassium fluoride which may be again electrolysed Hence a small quantity of the double fluoride can serve for the decomposition of a comparatively large amount of hydrofluoric acid.

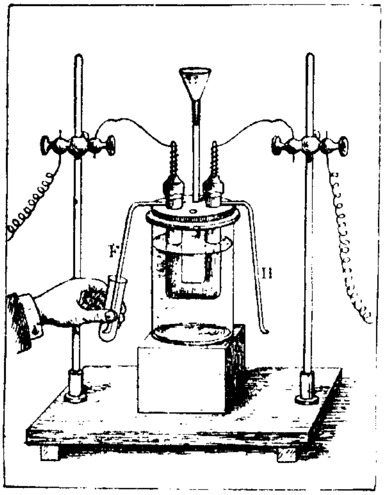


FIG. 3.

To prepare the pure anhydrous acid, a known volume of commercial acid was treated with sufficient potassium carbonate to neutralise about a fourth part, and was then distilled in a leaden retort over an oil-bath at 120°. Potassium fluosilicate, formed from the hydrofluosilic acid contained as impurity, was not decomposed on distilling, and the distillate was therefore free from silica. The distillate was divided into two parts, one of which was neutralised by potassium carbonate and then added to the other half, thus forming the double fluoride HF·KF. This was dried at 100°, and kept for several days in vacuum in the receiver of the air-pump, over sulphuric acid and sticks of potash. When perfectly dry, this compound falls to powder, and is then ready for the preparation of the anhydrous acid. The dry fluoride thus obtained was introduced into a platinum retort and gently heated; the first portions of distillate are rejected, as they contain traces of water. A platinum receiver is then adapted and placed in a freezing mixture of ice and salt: on increasing the temperature, pure hydrofluoric acid passes over and is condensed in the receiver as a limpid liquid, which boils at 19·4°, is very hygroscopic, and fumes in air (Ann. Chim. [6] 12, 472–537).

The double fluoride is very soluble in hydrofluoric acid, forming with it a crystallisable compound richer in hydrofluoric acid than the double fluoride itself, and which gives off no acid vapour at the boiling-point of the anhydrous acid (19·4°).

Moissan electrolysed the double fluoride itself, which fuses at 140° to a colourless liquid. The experiment was done, as before, in a U-tube of platinum, but the latter was strongly attacked. On dipping the platinum terminals of the battery into the fused double fluoride contained in a platinum dish, gas was freely evolved at each pole, detonation occurring on bringing the terminals together, even in the dark. The wire at the end where the fluorine was evolved was strongly corroded.

Later Moissan found it possible to use an apparatus made of copper. The metal becomes coated with a film of fluoride CuF_2, which is insoluble and protects the copper from further corrosion. The electrodes must be made of platinum instead of copper, as the fluoride formed on the latter would diminish the current (Compt. rend. 1899, 128, 1543–1545).

For the preparation of anhydrous hydrogen fluoride sodium hydrogen fluoride is preferable to the potassium salt.

Fluorine can be prepared in quantity by the electrolysis of fused potassium hydrogen fluoride. A stout cylindrical copper cell, 3½ inches diameter by 8 inches deep, heated electrically by a nichrome winding, is used. The cell itself acts as a cathode and a graphite rod as anode. The evolution of fluorine occurs at 240°–250° with a current of 10 ampères at 12 volts (Argo, Mathers, Humiston and Anderson, Amer. Electrochem. Soc. 1919). For a modification of this process *see* Meyer and Sandow, Ber. 1921, 54 [B], 759.

Properties.—Fluorine is a gas of a penetrating and disagreeable smell, similar to that of hypochlorous acid. A column of the gas enclosed in a platinum tube 50 cm. long, with colourless fluorspar ends, has a decided greenish-yellow colour (Moissan, Compt. rend. 1890, 109, 937–940). Its dispersion is anomalous, being less at the blue end of the spectrum than it is at the red (J. H. Gladstone and G. Gladstone, Phil. Mag. 1891, [5] 31, 1–9).

The atomic refraction of fluorine, as determined from a number of its compounds for the line H of the solar spectrum, varies from 0·35 to 0·63, the numbers for chlorine, bromine, and iodine being 10·0, 15·2, and 25·2 respectively (Gladstone, *l.c.*). For sodium light, the values 1·082 in unsaturated and 0·775 in saturated compounds (calculated according to the Lorentz formula) have been obtained by Swarts (Chem. Zentr. 1897, ii. 1042–1043). The atomic refraction of fluorine in unsaturated bodies is thus almost equal to that of hydrogen, so that if a double link is really present, fluorine has the smallest atomic refraction of any known element, its magnitude corresponding to its extremely low atomic volume, shown by Traube to lie between 0 and 1 (Annalen, 1896, 290, 105). The refractive index of the free element is 1·000195 for sodium light, being thus almost exactly one quarter that of chlorine, and bearing the same relation to it as do the refractive indices of nitrogen, oxygen, and neon to those of phosphorus, sulphur and argon respectively. This value was obtained directly from measurement of the electrolytic gas, due allowance being made for oxygen, ozone, and nitrogen, which are always present (Cuthbertson and Prideaux, Phil. Trans. 1905, 205, A, 319-331).

The density of fluorine was determined after purification of the gas by passing it through a platinum worm cooled to −50° by methyl chloride, and thence through a tube containing anhydrous sodium fluoride, which removes the last traces of hydrogen fluoride. The volume of the gas was determined by analysis after interaction with water. The first determination was made in platinum vessels, and gave the value 1·265 (air) (Moissan, Compt. rend. 1890, 109, 861–864), but a later value, 1·310, obtained by the Regnault method in a glass vessel (Moissan, *ibid.* 1904, 138, 728-732), corresponds almost exactly to the value 1·319, calculated from the atomic weight F 19·05 and molecular weight 38·10. The possibility of the existence of any measurable proportion of free fluorine atoms is thus excluded.

Fluorine was liquefied by Moissan and Dewar in 1897 (Compt. rend. 1897, 124, 1202–1205) by subjecting the gas to the cooling action of liquid oxygen, boiling under reduced pressure. Liquid fluorine is of a yellowish colour and very mobile. When placed in liquid hydrogen, it forms a white solid, m.p. 223° (Moissan and Dewar, Compt. rend. 1903, 136, 641–643). The critical temperature of fluorine is about 120°; the critical pressure, about 40 atmospheres; and the boiling-point, −187°. The density of liquid fluorine is about 1·14. Its specific refraction is greater than that of liquid air or oxygen, its capillary constant less than that of liquid oxygen. It has no magnetic properties, and shows no specific absorption bands (Moissan and Dewar, Chem. Soc. Proc. 1897, 175).

Fluorine gas has an irritating effect on the eyes and upon the mucous membrane. It decomposes water with formation of hydrofluoric acid, and the oxygen which is set free is ozonised. It corrodes glass, and attacks with violence all organic compounds, cork being at once carbonised and inflamed; alcohol, ether, benzene, and turpentine take fire immediately in contact with it.

Fluorine, freed from hydrofluoric acid by subjection to the temperature of boiling air and subsequent passage over dry sodium fluoride cooled by a solution of solid carbon dioxide in acetone, does not attack glass even at 100°, provided that the surface of the glass is free from all traces of organic matter. It is impossible to dry fluorine by means of phosphorus pentoxide, as phosphoryl trifluoride is immediately formed (Moissan, Compt. rend. 1899, 129, 799–804).

Fluorine combines with hydrogen, even in the dark, the combination is attended with detonation, and is effected even at the temperature of liquid hydrogen (Moissan and Dewar, *ibid.* 1903, 136, 641–643). Iodine burns in fluorine with a pale-blue flame, forming iodine pentafluoride (Moissan, *ibid.* 1902, 135, 563), and, in an atmosphere of iodine vapour, fluorine burns with a similar flame. Vapour of bromine loses its colour in fluorine, and the combination is sometimes attended with detonation with formation of bromine trifluoride (Lebeau, *ibid.* 1905, 141, 1015; Prideaux, Chem. Soc. Trans. 1906, 316). Fluorine at once releases chlorine from cold potassium chloride; chlorine is also expelled from its combination with carbon in carbon tetrachloride, but does not unite with fluorine.

Nitrogen also has no action on the gas, but excess of fluorine acts upon nitric oxide at the temperature of liquid oxygen, forming nitroxyl fluoride, m.p. −139°, b.p −63·5°, density 2·17 2·31, a colourless gas at the ordinary temperature (Moissan and Lebeau, Compt. rend. 1905, 140, 1621-1626).

Sulphur, selenium, and tellurium, on being placed in fluorine, at once melt and inflame with incandescence and formation of fumes and a coating of solid fluorides. Phosphorus burns in it with formation of fluoride and oxyfluoride; arsenic in powder becomes incandescent, and forms liquid drops of the trifluoride; antimony also becomes incandescent. Silicon in crystalline form, and cold, burns with brilliancy, and sometimes with scintillations. Adamantine boron also burns in the gas.

Metals are all attacked, but with varying energy, and formation of fluorides. Sodium and potassium in the cold are rendered incandescent. Calcium, magnesium, and aluminium become incandescent when slightly warmed. Iron and manganese in a state of powder, with slight warming, burn with bright scintillations. Lead is attacked in the cold, and tin on slightly warming. Mercury is entirely converted into a yellow protofluoride. Silver, at a gentle heat, becomes coated with a satin-like deposit of fluoride soluble in water. Gold and platinum, when heated to between 300° and 400°, become converted into their respective fluorides, which are decomposed again at a red heat with evolution of free fluorine (Ann. Chim. 1887, [6] 12, 472–537: Moissan, Fluorine et ses composés). Even at −187°, liquid fluorine reacts with a large number of substances. Sulphur, selenium, arsenic, phosphorus, potassium; calcium oxide, and anthracene all react violently with it, while solid fluorine combines with liquid hydrogen at −252·5°, with violent explosion, sufficient heat being evolved to render the materials incandescent (Moissan and Dewar, Compt. rend. 1903, 136, 641-643). If, however, sulphur, phosphorus, carbon, silicon, boron, and iron be first cooled in liquid air, they do not react with fluorine at −185°, neither is iodine displaced from iodides at this temperature, nor glass corroded (Moissan and Dewar, *ibid.* 1897, 124, 1202–1205). If fluorine be passed into liquid oxygen, a flocculent precipitate collects, which deflagrates on rise of temperature. It is probably a hydrate of fluorine, as it is never obtained from perfectly dry oxygen.

The majority of the metallic compounds of fluorine are easily fusible, and when ignited in a current of steam many of them are converted into the corresponding oxides, whilst hydrofluoric acid is formed. The fluorides of silver and tin are easily soluble in water, while those of sodium, potassium, and iron are only sparingly soluble. They are all decomposed by sulphuric acid when heated, with evolution of hydrofluoric acid, but nitric does not so easily attack them. Heated in a current of chlorine, they are all decomposed with formation of corresponding chlorides. Solutions of the soluble fluorides corrode glass, and they give no precipitate with silver nitrate, as the fluoride of silver is soluble. Lead, barium, magnesium, and calcium salts produce insoluble precipitates. The precipitate of calcium fluoride is so transparent as to be perceived with difficulty, but is rendered more opaque by heating.

Many metallic fluorides combine with hydrofluoric acid and form compounds obtainable in crystals soluble in water. The double fluorides of the alkali-metals with the fluorides of the electro-negative metals which form acids with oxygen may be obtained with facility, and are analogous in composition to the double fluoride of hydrogen and potassium. They are all decomposed by sulphuric acid, yielding hydrofluoric acid and a sulphate. A mixture of hydrofluoric acid and nitric acid dissolves silica which has not been previously ignited, but the mixture has no action on gold or platinum.

The atomic weight of fluorine.—With notable exceptions, all the determinations of the atomic weight of fluorine involve the conversion of fluorides of various metals into the corresponding sulphates, the fluoride most commonly employed being that of calcium, which was used in some cases in the form of a very pure fluorspar.

Berzelius (Poggendorff's Annalen, 1826, 8, 1), Louyet (Ann. Chim. 1849, [3] 25, 295), Dumas (Annalen, 1860, 28, 113), De Luca (Compt. rend. 1860, 51, 299), and Moissan (*ibid.* 1890, 111, 570–572) all made use of this method, the average weight of calcium sulphate obtained from one part of fluoride being 1·7444±0·00018 gram, which gives 18·999 as the atomic weight of fluorine.

Louyet, by the conversion of lead fluoride into lead sulphate, obtained the value 19·01; Moissan, working with barium fluoride, obtained the value 19·02. Dumas, Louyet, and Moissan (Compt. rend. 1890, 111, 570–572) also worked with sodium fluoride, the results by this method being uniformly higher, viz. 19·08, 19·06, and 19·07 respectively. Values were also obtained by Dumas and Moissan from the conversion of potassium fluoride into potassium sulphate.

An exceptional method was employed by Christensen (J. pr. Chem. 1886, [2] 34, 41–46), who took advantage of the decomposition of ammonium manganifluoride $(NH_4)_2MnF_5$ to measure the atomic weight of fluorine. The manganifluoride was treated with potassium iodide, one molecule of the former, on acidification with hydrochloric acid, liberating a molecule of iodine, which was then titrated with standard sodium thiosulphate solution. In the first series of experiments, he obtained the value F=19·00, and in the second (J. pr. Chem. 1887, [2] 35, 541–559) F=18·99.

Meyer (Zeitsch. anorg. Chem. 1903, 36, 313–324) compared the results of these previous investigations, criticising both the suitability of the methods and the purity of the materials employed. To the latter cause he mainly attributed the discrepancies in the values obtained. He therefore started with pure ammonium carbonate and calcium nitrate, converted the calcium carbonate so obtained into oxide, which he slaked and converted into chloride, and passed finally to fluoride by evaporation of the chloride with specially purified hydrofluoric acid. As the mean of 5 determinations, he obtained the value F=19·036, error ±0·00149. The general mean of all the determinations agrees well with the results of Christensen and Meyer, if all the values are recalculated with the most recent atomic weights (F. W. Clarke, Recalculation of Atomic Weights, 1910). The mean value for the atomic weight of fluorine is 19·041 ± 0·00135; the recalculated results of Christensen give an average value of 19·038, and those of Meyer 19·035.

Additional confirmation of Christensen's value is obtained from the fact that the atomic weight of manganese, Mn=54·933, calculated from his data, agrees well with that obtained by Baxter and Hines (J. Amer. Chem. Soc. 1906, 28, 1560).

Smith and van Haagen find F=19·002. Moles and Patuecas (Journ. Chim. Phys. 1919, 17, 538), by determining the weight of a normal litre of methyl fluoride, find F=18·996.

Comparison of fluorine with the other halogens.—Fluorine is by far the most energetic member of the halogen family, and, as is frequently the case with the first member of a series, it possesses very distinctive properties. Moissan has pointed out (Bull. Soc. chim. 1892, [3] 5, 880–885) that in certain of its relations, it remotely resembles oxygen rather than chlorine. Thus carbon readily takes fire and burns in it (Moissan, Compt. rend. 1890, 110, 276–279). Calcium fluoride is very different from calcium chloride, rather resembling calcium oxide in solubility. Silver fluoride is also anomalous, being easily soluble in water, while aluminium fluoride is much less easily hydrolysed than is the chloride.

Fluorine compounds with the non-metals are uniformly more volatile than the chlorine compounds, but the metallic fluorides usually require a higher temperature for fusion than do the other halides.

The boiling-point of a hydrocarbon is increased on the average by 5° by the substitution of fluorine for hydrogen, but if fluorine is introduced into a molecule already containing halogen atoms, the boiling-point is lowered, the same behaviour being observed in the case of aldehydes. In this respect, fluorine differs greatly from chlorine (Henry, Rec. trav. chim. 1897, 16, 218–225; Moissan and Dewar, Chem. Soc. Proc. 1897, 175).

Hydrofluoric acid or Hydrogen fluoride HF. The corrosive action of this compound on glass was known to Schwanhardt of Nuremberg as early as the year 1670. Scheele, in 1771, first recognised that fluorspar is a compound of lime and a peculiar acid, and he prepared the latter in both the aqueous and gaseous forms by distilling in a tin retort. Priestley was the first to collect the gas over mercury. It was regarded by Gay-Lussac and Thenard, in 1808, as an oxygen compound. Ampère, however, in 1810, pointed out its similarity to hydrochloric acid, a view which was subsequently supported and confirmed by Davy and Berzelius. It was first obtained in a pure state by Gore in 1868.

Its volumetric composition can be shown either by electrolysing the acid and collecting and measuring the liberated hydrogen and oxygen, or by allowing a measured volume of fluorine to act on water, titrating the acid formed, and measuring the oxygen. In both cases, after allowing for the contraction in the volume of oxygen, due to formation of ozone, the results show that hydrogen fluoride is formed by the union of equal volumes of hydrogen and fluorine (Moissan, Compt. rend. 1900, 130, 544–548; *cf.* mol. wt., Gore, below).

The anhydrous acid is best prepared from the double fluoride of potassium and hydrogen, as previously described. Fremy obtained the anhydrous acid by decomposing lead fluoride with dry hydrogen.

Anhydrous hydrofluoric acid is a colourless, mobile liquid of density 0·9879 (Gore). It boils at 19·4°, and solidifies at −102·5° to a white crystalline transparent mass, becoming white and opaque at a lower temperature, and melts at −92·3° (Olszewski, Monatsh. 1886, 7, 371–374). Its vapour tension at 15·5° is equal to a pressure of 7·58 lbs. per square inch. The anhydrous acid does not attack glass even if left in contact with it for weeks; but if the least trace of moisture be present, this action is apparent at once. The acid has little action on the metalloids and the noble metals, and below 20° the other metals are not attacked. Basic oxides unite readily with it, some of them dissolving; on peroxides it has no effect.

Potassium, when thrown into the anhydrous acid, decomposes it with explosion. It combines eagerly with phosphoric and sulphuric anhydrides, with evolution of great heat, in this respect resembling water, and not its more obvious analogue, hydrochloric acid. It also combines energetically with the fluorides of potassium and sodium, just as water combines with the oxides of these metals.

The anhydrous acid decomposes carbonates with effervescence and with the formation of fluorides. Solid organic bodies immersed in it are for the most part disintegrated. Gutta-percha, caoutchouc, and numerous gums and resins dissolve to red liquids. Guncotton, silk, paper, cotton wool, calico, &c., are converted into glutinous substances, and generally dissolve. Wood spirit, alcohol, and ether, but not benzene, mix with it, and oil of turpentine, when mixed with it, forms a red liquid (Gore, Proc. Roy. Soc. 17, 256).

Hydrogen fluoride, at a white heat, converts aluminium oxide into the fluoride. Yttrium oxide and lanthanum oxide are converted into non-volatile fluorides. Finely divided quartz is completely volatilised without the action of heat; with titanium, zirconium, columbium, and tantalum oxides a red heat is necessary (van Haagen and Smith, J. Amer. Chem. Soc. 1911, 33, 1504).

The molecular weight of hydrogen fluoride has been a source of some controversy. Gore (Phil. Trans. 1869, 73) showed that the volume of hydrogen fluoride gas obtained by the action of hydrogen on silver fluoride was twice that of the hydrogen taken, the measurements being made at 100°, but Mallet, weighing the gas at 30·5° in a large flask coated with paraffin, obtained a value for the density corresponding to a molecular weight of 39·32, which indicates the molecular formula H_2F_2 (Amer. Chem. J. 1881, 3, 189).

Thorpe and Hambly (Chem. Soc. Trans. 1889, 163) found that the vapour density of hydrogen fluoride varies rapidly with the temperature and pressure. The following table gives the results of their experiments at temperatures varying between 26·4° and 88·1°:—

Temperature	Pressure mm.	V.D. air = 1	Mol. weight
26·4°	745	1·773	51·18
27·8	746	1·712	49·42
29·2	750	1·578	45·54
32·0	743	1·377	39·74
33·1	750	1·321	38·12
33·8	758	1·270	36·66
36·3	739	1·115	32·20
38·7	751	1·021	29·46
39·2	743	1·002	28·94
42·8	741	0·910	26·26
47·3	745	0·823	23·76
57·5	750	0·737	21·28
69·4	746	0·726	20·96
88·1	741	0·713	20·58

These numbers show that the process of dissociation of the vapour of hydrogen fluoride is perfectly continuous, and that there is no direct evidence of the existence of a molecule corresponding to H_2F_2. It is also found that the vapour density is lowered by diminishing the pressure of the gas at a constant temperature. The following table shows the vapour density of hydrogen fluoride under varying pressures at the constant temperature of *circa* 32°:—

Temperature	Pressure mm	V.D. air = 1	Mol. weight
32·0°	743	1·377	39·74
32·2	686	1·239	35·78
31·8	655	1·177	33·98
32·0	603	1·068	30·82
32·5	545	0·963	27·78
32·3	498	0·920	26·54
31·9	354	0·797	23·00
32·3	353	0·789	22·78

Similar results were obtained by mixing the hydrogen fluoride with air so as to lower the partial pressure of the gas.

The anhydrous acid, on addition of water, is changed in sp.gr. from 0·988 to as much as 1·25, further dilution causing a regular decrease in sp.gr. (For a table showing the relation between the sp.gr. and strength of hydrofluoric acid, *v.* Winteler, Zeitsch. angew. Chem. 1902, 15, 33–34; J. Soc. Chem. Ind. 1902, 277.) The acid of sp.gr. 1·15 may be distilled unchanged; it boils at 120°, and contains about 36 to 38 p.c. of the anhydrous acid, but does not thus form a definite hydrate; when allowed to evaporate over caustic lime in the air, the aqueous acid attains a constant composition containing 32·6 p.c. of the anhydrous acid (Roscoe, Chem. Soc. Trans. 1861, 13, 162).

According to Deussen (Zeitsch. anorg. Chem. 1906, 49, 297–300), a constant boiling mixture of boiling-point 111° at 750 mm. pressure has a sp.gr. of 1·138 at 18° and contains 43·2 p.c. hydrofluoric acid by weight.

Hydrogen fluoride gas is formed from its elements with great evolution of heat:

H gas + F gas = HF gas + 37·6 cals.

H gas + F gas = HF (dissolved) + 49·4 cals.

(Berthelot and Moissan, Compt. rend. 1889, 109, 209). (For heat of dissolution, *cf.* Guntz, Bull. Soc. chim. 1884, 40, 54–57.) The dilution of acid containing more than two molecules of water does not produce a sensible evolution of heat, as does similar dilution of the other halogen acids (Guntz, *l.c.*)

Hydrofluoric acid is also unique in that it combines with its own salts with absorption of heat NaF+HFAq. = −228 (Thomsen). The freezing-point of water is depressed by hydrofluoric acid, and quantitative determinations point to the existence of molecules of H_2F_2 in solution (Abegg, Fox, and Herz, Zeitsch. anorg. Chem. 1903, 35, 129–147; Paternò and Peratoner, Chem. Zentr. 1891, 306).

This view is supported by the fact that the heat of dissociation of hydrofluoric acid is 3550 cals., which is three times the corresponding value for hydrochloric acid, and is most easily explained by assuming the preliminary dissociation $H_2F_2 \rightleftharpoons 2HF$ (Abegg, Ber. 1900, 33, 393–394), and further evidence is obtained from the fact that by the application of Ostwald's basicity rule, the value for the basicity =2·08. This observation is confirmed by measurements of specific conductivity after the addition of successive quantities of potassium, sodium, and ammonium hydroxides (Pellini and Pegoraro, Zeitsch. Elektrochem. 1907, 13, 621). Acid, containing 55 p.c. hydrogen fluoride, cooled to −45°, is converted into small truncated prisms, having the composition HF,H_2O and melting at −35° (Metzner, Compt. rend. 1894, 119, 682–684). Other evidence as to the existence of hydrates is derived from the relation of the specific conductivities of different solutions of hydrofluoric acid to the corresponding concentrations. It is found that breaks in the curve obtained by plotting these values occur at concentrations of 91 p.c., and between 51 and 55 p.c. corresponding to the hydrates 9HF, H_2O, and HF,H_2O (*cf.* Metzner, *l.c.*; Hill and Sirkar, Proc. Roy. Soc. 1909, A, 83, 130–148).

The temperature coefficient of conductivity for solutions containing less than 7·7 p.c. HF =0·0125 and is constant. Hydrofluoric acid can be electrolysed with platinum as a positive electrode, the products being hydrogen, oxygen, and ozone, but with acid of 30 p.c. strength, the platinum is attacked.

The dilute acid dissolves all the metals except platinum and some of the metals associated with it—gold, silver, lead, and mercury—with evolution of hydrogen. On this account, it is kept in platinum vessels when concentrated, and in leaden or guttapercha vessels in the dilute form.

Aqueous hydrofluoric acid may be kept in glass bottles coated with a film of guttapercha as follows. Guttapercha is dissolved in carbon disulphide and the solution put in a bottle, every part of the interior of which must be brought in contact with the solution; the excess, if any, is then poured out, and the bottle laid aside until the solvent has volatilised. Caoutchouc stoppers are required (Chem. News, 49, 201).

On mixing one part of finely powdered and pure fluorspar with about twice its weight of strong sulphuric acid, no evolution of gas takes place at ordinary temperatures, but a transparent gelatinous mass is formed, and, on gently heating, dense and highly irritating fumes arise, somewhat similar to those produced in the manufacture of hydrochloric acid: $CaF_2+SO_4H_2=SO_4Ca+2HF$. For ordinary purposes, the decomposition is effected in a leaden retort, divided into two halves for convenience in cleaning, which, when in use, are accurately fitted together by an overlapping grooved joint. The receiver may be a leaden V-tube, blind at one end, and fitted by grinding at the other to the neck of the retort; the retort is heated on a sand-bath, and the acid is condensed in the receiver, which is surrounded by a freezing mixture.

According to Ruff and Braun (Ber. 1914, 47, 646), it is best to use 90 p.c. sulphuric acid. When 97–100 p.c. is used, a yield of 60 p.c. of hydrofluoric acid is obtained; this acid is of 95–96 p.c. strength. When sulphuric acid containing a high percentage (50–60 p.c.) of sulphur trioxide is used, the product consists of *fluorosulphonic acid*:

$$CaF_2+H_2SO_4+2SO_3=CaSO_4+2F{\cdot}SO_2{\cdot}OH$$

first obtained by Thorpe and Kirwan by the action of liquid hydrogen fluoride on liquid sulphur trioxide (Chem. Soc. Trans. 1892, 61, 921). It is a thin colourless liquid fuming in the air and boiling at 162·6° (*v.* FLUOROSULPHONIC ACID).

To prepare the aqueous solution on a large scale, a leaden retort, on the upper part of which a leaden head can be cemented, is used; the neck of the retort fits into the side of a leaden receiver or chamber, in which is placed a basin of water. The acid vapours are absorbed by the water, and air, with any excess of acid vapours, is conducted through an escape pipe into the atmosphere.

The impure commercial acid may be purified by passing an excess of hydrogen sulphide through the liquid, neutralising the sulphuric and silicofluoric acids present with potassium carbonate, then decanting and adding silver carbonate to remove excess of hydrogen sulphide, filtering, distilling the filtrate from a leaden retort with a platinum receiver, and finally rectifying. As in the case of fluorine itself, copper can readily be employed as the material of the containing vessels (Goldschmiedt, Monatsh. 1907, 28, 297–298).

Use of hydrofluoric acid.—The chief use of this compound is in etching glass. In making the graduations on a thermometer the tube is first coated with engravers' etching varnish; the divisions are then accurately traced with a fine-pointed instrument through the varnish. The tube is then plunged for a short time into a long tube containing dilute hydrofluoric acid, when, after cleaning the thermometer tube, it will be found to be permanently engraved. If the engraving is done by the vapour of hydrofluoric acid, the tracings are white and opaque, whereas if the liquid acid be employed, the lines are transparent.

There are three processes in use for the preparation of opaque etchings on glass: viz. (*a*) the application of solutions of acid fluoride of the alkalis; (*b*) a mixture of fluorspar with sulphuric acid; and (*c*) hydrofluoric acid gas. The first of these always contains uncombined hydrofluoric as well as an indifferent salt as shown in the following recipes :—

	I.	II.		III.	
	grms				
Water . . .	1000	100	1000	1000	1000
Acid potassium fluoride . .	250	—	—	—	—
Sodium fluoride .	—	—	40	250	—
Ammonium fluoride	—	—	—	—	1000
Alkali fluoride .	—	8	—	—	—
Hydrochloric acid .	250	—	—	160-175	-
Sulphuric acid .	-	1	—	—	250
Glacial acetic acid .	-	—	50	—	—
Potassium sulphate	140	—	—	200	—
Ammonium sulphate	—	—	—	—	100

The first of these recipes is recommended by Tessié du Mothay and Maréchal; the two under heading II. by Siegwart, and those under heading III. by J. B. Miller. In practice, however, an acetic solution of sodium fluoride is much used, and is prepared by dissolving 25 parts of sodium carbonate crystals in 5 parts of fuming hydrofluoric acid, and adding to 1 litre of this solution after clarifying, 1 litre of glacial acetic acid. For light shades of etching, a single application of the acid is sufficient, but for deeper shades repeated applications are necessary, as is the case in etching landscapes, &c., on glass. An etched glass surface viewed by the microscope has the appearance of an aggregation of crystals, hexagonal in shape, and agrees with those of silicon-sodium fluoride, and in addition there are some longer in shape, which much resemble those of silicon-calcium fluoride. Small crystals are formed from concentrated solutions, and the smaller the crystals the more delicate is the etching. The strength of an etching solution must be varied according to the compound used, and regard must also be paid to the kind of glass to be operated upon. The application of gaseous hydrofluoric acid does not produce a uniform opacity, and is, therefore, not suitable for the production of opaque plates (J. Soc. Chem. Ind. 5, 669).

It has been suggested that hydrofluoric acid should be employed in the purification of beet sugar, the alkalis present in the juice being effectually removed by the acid, whilst the organic matter remains unaffected (*cf.* Verbiese, J. Soc. Chem. Ind. 1900, 160).

Antiseptic properties of fluorine compounds.—W. Thompson found that the compounds of fluorine, such as hydrofluoric acid, the acid and neutral fluorides of sodium, potassium, and ammonium (as well as the fluosilicates of these bases), are effectual as antiseptics. Free hydrofluoric acid retards the activity of yeast, 5·5 mgm. per 100 c.c. of saccharine solution arresting fermentation. Potassium fluoride, up to the same strength, however, augments it (Effront, Bull. Soc. chim. 1891, [3] 5, 476–480). The free acid promotes the activity of diastase by retarding lactic and butyric fermentations (Effront, *ibid.* 1891, 4, 337–339; 627–632; 1892, 6, 786–793), and its application in breweries has been suggested (Just, J. Soc. Chem. Ind. 1902, 131). Acid ammonium fluoride is especially used for disinfecting rubber hose-pipes in breweries, as it is a powerful antiseptic and does not attack the rubber (Schonfeld, J. Soc. Chem. Ind. 1901, 830; Brand, *ibid.* 1904, 265; Bidtel, *ibid.* 1904, 620).

Fluorides have also been used as preservatives for sweet wines and beer, sodium fluoride having been put on the market for this purpose under the name 'Remarcol.'

Tests for hydrofluoric acid.—For the detection of this compound, its corrosive action on glass is utilised. The compound suspected to contain a fluoride is reduced to powder and moistened with strong sulphuric acid in a platinum or leaden capsule. A watch-glass is thinly coated with wax, and, after tracing some design with a sharp-pointed instrument, is inverted over the capsule. The capsule is then gently warmed and the watch-glass placed over it, a little water being put in to prevent the melting of the wax. On removing the watch-glass after a few minutes' exposure, and cleaning off the wax with a little oil of turpentine, the parts exposed will have become etched if fluorine was present in the mixture. When the etching is very faint, a good plan is to breathe upon it, which makes the markings more apparent.

In the absence of boron, this test can be made more delicate by placing the suspected substance, mixed with quartz powder and a little magnesite, in a test-tube fitted with a cork, carrying a glass rod having a knob at the lower end. This knob is painted black and a drop of water is placed on it. On adding conc. sulphuric acid to the mixture in the tube and warming cautiously, a white film will be seen if as little as 0·1 mgm of fluorine is present (Daniel, Zeitsch. anorg. Chem. 1904, 38, 257).

For the detection of fluorine in butter, the aqueous portion from 50 grams of melted butter is treated with calcium chloride solution and a small excess of sodium carbonate. The resulting precipitate, consisting probably of borate, carbonate, phosphate, sulphate, and fluoride, is extracted with acetic acid, ignited and heated on a sand-bath with sulphuric acid, under a waxed watch-glass cooled by water on its upper surface for 2 hours. 1 mgm. of calcium fluoride will, under these circumstances, give a distinct etching on glass (Hehner, Analyst, 1902, 27, 173–179).

For methods of estimating fluorine *v.* ANALYSIS.

A gravimetric and volumetric estimation of fluorine, depending upon Pisani's method of precipitation as thorium fluoride, has been devised by Gooch and Kobayashi (Analyst, 1918, 360).

Silicon fluoride may be estimated by measurement, in a dry gas burette, of the volume of gaseous silicon fluoride produced by the interaction of quartz, fluoride, and sulphuric acid (Oeltel, Zeitsch. anal. Chem. 1886, 25, 505; Hempel and Scheffler, Zeitsch. anorg. Chem. 1899, 20, 1–11).

Hydrofluoric acid may be estimated by the amount of etching produced (Ost, Ber. 1893, 26, 151; Wislicenus, Zeitsch. angew. Chem. 1901, 706; Leiniger, Chem. Zeit. 1902, 26, 967; Woodman and Talbot, J. Amer. Chem. Soc. 1906, 28, 1437–1443).

Fluorine in soluble fluorides can be estimated volumetrically by taking advantage of the fact that ferric fluoride, unlike ferric chloride, does not liberate iodine from iodides. The liquid is acidified with hydrochloric acid, mixed with a known excess of ferric chloride solution, then with excess of zinc iodide, allowed to remain in a closed vessel at 35°–40° for half an hour, and the liberated iodine titrated with sodium thiosulphate solution (Knobloch, Chem. Zentr. 1894, ii. 533–534).

For the estimation of fluorine in wine, a standard method has been worked out, as fluorine preservatives are so frequently used. 100 c.c. of wine are made feebly alkaline with sodium hydroxide, silver nitrate is added, so long as it produces a precipitate, and the solution made up to 250 c.c. and filtered. 200 c.c. of the filtrate are treated with excess of sodium chloride, made up to 250 c.c. and left for 24 hours. 175 c.c. of clear liquid are treated with 3–4 c.c. 2N-sodium carbonate solution and precipitated with a large excess of calcium chloride solution and boiled for 5 minutes. The precipitate is collected and ignited and digested with 24 c.c. of 3/2N-acetic acid until its weight is constant within 5 milligrams. For each 100 c.c. of washings, 0·0016 gram is added to correct for solubility (F. P. Treadwell and Koch, Zeitsch. anal. Chem. 1904. 43, 469–506). For beer, a slight modification of Penfield's method (Chem. News, 1897, 39, 79–180) has been recommended.

Silicofluoric acid or **Hydrofluosilic acid** H_2SiF_6. This compound is prepared by heating a mixture of sulphuric acid and fluorspar, sand, or powdered glass in a flask and passing the evolved silicon fluoride into water $3SiF_4+2H_2O=SiO_2+2(H_2F_2 \cdot SiF_4)$. The tube from which the fluoride escapes must dip into mercury at the bottom of the vessel of water, otherwise it would soon be stopped up by the deposition of silica. The bubbles of gas as they rise through the water are decomposed, and a gelatinous mass accumulates. The solution of acid is strained through linen to separate the silica, and is then filtered and concentrated at a low temperature. The acid is obtained more easily when required in quantity by dissolving silica in dilute hydrofluoric acid. The saturated solution fumes strongly, and has a very sour taste. It does not attack glass, but if allowed to evaporate on it the glass is attacked, especially on heating; silicon fluoride is volatilised, and the free hydrofluoric acid attacks the silica of the glass. The salts are called silicofluorides or fluosilicates, are generally soluble in water, and may be obtained well crystallised. The potassium salt is one of the least soluble salts of potassium, and the copper salt one of the most soluble of copper salts. Silicofluoric acid is sometimes employed as a test for potassium.

Hydrofluosilicic acid reacts with potassium ferrocyanide, especially in boiling solution, forming a greenish liquid, which, on contact with air, deposits a precipitate of Prussian blue. The same reaction takes place with the ferricyanide, but in the absence of air (Materschek, Chem. Zeit. 1901, 25, 158; 327). Calcareous stone surfaces can be hardened by means of a fluosilicate of some metal which forms an insoluble oxide, such as magnesium, aluminium, or lead. Carbon dioxide is given off, and calcium fluoride, silica, and alumina, or the carbonate of lead or magnesium fluoride, are formed, and the surface rendered hard and insoluble (Kessler, Compt. rend. 1883, 96, 1317–1319).

For modes of estimating hydro-fluosilicic acid *v.* ANALYSIS.

Antiseptic properties.—The fluosilicates possess more powerful antiseptic properties than the fluorides. They are not poisonous, possess no smell, and are sparingly soluble in water. As they have only a very slight alkaline taste, they may be employed for preserving food without communicating any taste to it.

They have been used in surgical operations. A solution containing 0·61 p.c. of ammonium fluosilicate is not irritating to wounds, whilst it possesses greater antiseptic power for animal tissues than 1 part of mercuric chloride in 1000 of water, which latter is a stronger solution than that which can be generally employed for surgical purposes without producing poisonous effects (Chem. News, 56, 132) (*v.* DISINFECTANTS).

A solution of free hydrofluosilicic acid containing 26 p.c. of the acid, has been placed on the market under the name Keramyl' (Prior, J. Soc. Chem. Ind. 1909, 904).

FLUOROCYCLENE $C_{48}H_{28}$. A hydrocarbon obtained by heating acenaphthene with lead oxide at 330°–340°. Crystallises in small orange-yellow triclinic rhombohedra, m.p. 396°–397° (Dziewonski and Saknarowski, Ber. 1918, 51, 457).

FLUOROFORM. A gas at ordinary temperatures, said to be obtained by heating a mixture of iodoform and silver fluoride (Valentiner and Schwarz).

FLUOROSULPHONIC ACID $F \cdot SO_2 \cdot OH$. First prepared by Thorpe and Kirman (Chem. Soc. Trans. 1892, 61, 921) by the action of hydrogen fluoride on sulphur trioxide. Is a colourless mobile liquid which fumes in the air and boils with slight decomposition at 162·6°. Has a faint pungent smell, and has but little action on the skin and feels greasy to the touch. It slowly attacks glass, more rapidly in presence of moist air. Is decomposed with almost explosive violence by water, but the decomposition, as shown by Traube, is not complete, as equilibrium exists between sulphuric and hydrofluoric acids on the one hand and fluorosulphonic acid and water on the other in not too dilute aqueous solution (Traube and Reubke, Ber. 1921, 54 [B], 1618). For salts of fluorosulphonic acid, see Traube, Ber. 1913, 46, 2525; Traube, Hoerenz, and Wunderlich, Ber. 1919, 52 [B], 1272. All the fluorosulphonates are freely soluble in water with the exception of the *nitron* salt, which forms pale green needles, m.p. 225°. In presence of mineral acids they are readily hydrolysed, but are more stable in alkaline solution. With aqueous ammonia they yield aminosulphates.

FLUOR-SPAR, *Fluor,* or *Fluorite.* (Ger. *Flussspat*; Fr. *Fluorine.*) A common mineral composed of calcium fluoride (CaF_2), crystallising in the cubic system. It is frequently found as well-developed crystals, usually cubes, but occasionally as octahedra; interpenetrating twinned cubes are common. An important character is the possession of perfect cleavages parallel to the faces of the octahedron. Sp.gr. 3·18; hardness 4 (the mineral can be scratched with a knife). The crystals have a bright vitreous lustre, and are frequently transparent; they may be colourless or various shades of purple, green, yellow, pink, &c., the mineral displaying a very extensive range of colour. Dull cleavage masses and massive material, sometimes quite compact or earthy, are of abundant occurrence.

The cause of the colour of fluor-spar has long been a subject of discussion, and although not yet definitely determined, it may, in some cases at least, be ascribed to the presence of traces of organic matter. Some crystals undergo a change in colour when exposed to sunlight; for example, certain greens are changed to purple. Changes in colour are also effected when the crystals are exposed to the cathode rays, or to the rays emitted by radium salts. Many crystals are decolorised when heated to a temperature ranging from 220° to 300°. The heating of the mineral is usually accompanied by a bright phosphorescence (thermo-luminescence), violent decrepitation, and the liberation of water and gases (carbon dioxide, carbon monoxide, hydrogen, nitrogen, argon, and oxygen). The water which distils off is sometimes brown, and has a strong 'empyreumatic' odour; and it is on this account, together with the fact that the mineral is decolorised at a low temperature, that the colour has been ascribed to organic matter. It must, however, be remarked that the water and gases, and possibly also any organic matter present, are contained in the fluor-spar in vast numbers of cavities, usually of microscopic dimensions, but sometimes large enough to show a moving bubble when a crystal is turned about in the hand. A remarkable phenomenon, sometimes associated with the colour of fluor-spar, is that of fluorescence; this is best displayed by certain purple or green crystals from Weardale, Co. Durham. A crystal, which by transmitted light is pinkish or greenish, exhibits when viewed in reflected light a rich plum-blue colour with a velvety softness which has the appearance of being diffused immediately beneath the surface of the crystal. This effect is destroyed when the crystals are heated to 220° or 300°.

Fluor-spar occurs under a variety of conditions: in cavities in granite rocks, in veins of tin-ore, occasionally as a cementing material in sandstone, and most abundantly as an associate of lead-ore in veins traversing limestone. Some of the veins in limestone, consisting almost entirely of pure massive fluor-spar, have a thickness of 20 feet. The whole of the production in England, amounting at the present time to about 40,000 tons per annum, is from north Derbyshire, and Weardale in Co. Durham, where it is obtained chiefly as a by-product in lead-mining. Formerly, when there was little or no demand for fluor-spar, this mineral was thrown out on the waste heaps; and now that the material is of value (10*s.* to 20*s.* per ton), these extensive waste heaps are being worked over. A considerable amount, some 50,000 tons per annum, is mined in the United States, principally in southern Illinois and western Kentucky. Curiously, however, a large portion of the English fluor-spar is exported to America. Smaller quantities are obtained in Bavaria, Saxony, France, and Spain.

The name fluor, from the Latin *fluo*, to flow, was used in the form *fluores lapides* by G. Agricola in 1529, and has reference to the use of this mineral as a flux in metallurgical operations. Within recent years, its application in this direction has been very considerably extended, and now large amounts are used in the manufacture of iron and steel, chiefly in the basic open-hearth process, and of ferrosilicon and ferromanganese. If not contaminated with too much silica (not over 3 or 4 p.c.), it acts better than limestone for fluxing; but it corrodes the furnace-linings, and the resulting slag contains less soluble phosphates available for fertilisers. To some extent, fluor-spar is also used in iron and brass foundry-work, as it produces a greater fluidity in the metal; in the smelting of lead-, copper-, silver-, and gold-ores; in the electrolytic refining of antimony and lead; and in extracting aluminium from bauxite. Other applications are in the glass and enamelling industries, and in the manufacture of opaline glass. In the form of sand, the mineral is used as a binding material in emery wheels and carbon-electrodes, and for mixing with mortar and cement.

Owing to its low refractive index ($\mu_D = 1\cdot43385$) and weak dispersion, clear and colourless fluor-spar is used with glass for the construction of the apochromatic lenses of microscope objectives, but material which is perfectly isotropic and sufficiently transparent and free from colour is difficult to obtain. German firms are said to have secured a supply from an unknown locality in Switzerland; and there is a fine specimen of clear colourless fluor-spar from Brienz, Switzerland, in the mineral collection of the British Museum. A limited amount of suitable material can be obtained by decolorising by heat the clear purple fluorescent cubes from Weardale, Co. Durham; and small colourless cubes are abundant in the neighbourhood of Matlock, Derbyshire. Suitable material in sufficient quantity is said to be found in Illinois; and a very promising deposit has been prospected in the Transvaal, between Zeerust and Mafeking. Material suitable for optical use has also been obtained at Madoc in Ontario.

A special variety of fluor-spar, known as 'blue-john,' for which the Tray Cliff cavern near Castleton in Derbyshire has long been famous, has been much used for fashioning vases and other small ornamental objects. Although occasionally used as a gem-stone on account of the delicate colouring, the mineral is much too soft for this purpose. Beads of fluor-spar have been found amongst prehistoric remains in North and South America.

Being the only common mineral containing fluorine in large amount (F 48·9 p.c.), fluor-spar is used for the preparation of hydrofluoric acid and other fluorine compounds. It is slightly soluble in hydrochloric acid and in solutions of alkali carbonates, and is readily decomposed by sulphuric acid even in the cold (on this depends its use for etching glass, a process in use long before the discovery of the element fluorine). Being almost the only substance not attacked by free fluorine, it was used by H. Moissan in the construction of his apparatus for the isolation of this element.

References.—Special Reports on the Mineral

Resources of Great Britain, Mem. Geol. Survey, 1916, vol. iv. Fluor-spar, Imp. Min. Res. Bur. London, 1921. On the fluor-spar deposits of Derbyshire, *see* C. B. Wedd and G. C. Drabble, Trans. Inst. Mining Eng. 1908, vol. 35, 501; on those of Weardale, *see* W. M. Egglestone, *tom. cit.* 236. On American deposits, *see* H. F. Bain, Bull. U.S. Geol. Survey, 1905, No. 255; E. O. Ulrich and W. S. T. Smith, Prof. Paper, U.S. Geol. Survey, 1905, No. 36; H. Ries, Economic Geology, New York, 1916. On the fluorescence, thermo-luminescence, and liquid and gaseous enclosures, *see* H. W. Morse, Proc. Amer. Acad. Sci. and Arts, 1906, vol. 41, p. 585; Blount and Sequeira, Chem. Soc. Trans. 1919, 115, 705. L. J. S.

FLUX. A term applied in metallurgy to the material which is added to a charge of ore for the purposes of combining with earthy or metallic impurities and removing them as slag, or to any substance which is fluid at a high temperature and protects the regulus from oxidation.

All ores contain gangue, either of an acidic (silicious) or of a basic character, which, if the ore were subjected to the action of a reducing agent alone, would retain a large proportion of the reduced metal and also foul the furnace. In order to remove the gangue and the accumulated impurities from the reduced metal, it is necessary to add materials which will combine with them to form a fusible slag.

A distinction may be made between the fluxes which are used for assaying and those which are used for smelting on a large scale, though even among the latter there are many special fluxes, *e.g.* antimony glass (*v.* ANTIMONY), for details concerning which the articles on the extraction of the several metals should be consulted.

The more important fluxes used in assaying are:

Sodium carbonate (or potassium carbonate, or a mixture of the two), which gives very fluid slags with acidic ores, and acts also as desulphurising agent.

Borax fluxes with basic materials, forming readily fusible borates of the metals. Borax has a marked influence in increasing the fluidity of most slags.

Fluorspar, used especially with phosphates, is a 'neutral' flux.

Litharge and **Red lead** are useful fluxes for oxides of iron or copper, &c.

Potassium cyanide, which acts chiefly as a reducing agent, being converted into cyanate. (For further details, *see* art. ASSAYING.)

The fluxes used on the large scale are few in number, as it is essential to the economic success of a process that the cost of slag-producing materials should be as low as possible. An economy is frequently effected by mixing together in proper proportions an ore in which the gangue is silicious in character with another containing basic impurities. In general, the character of the fluxes to be used must be decided by the nature of the ore, the object usually being so to arrange matters that the furnace charge shall contain basic and silicious constituents in the proportions required to form a fusible double silicate containing two bases. The proportion of silica present should be sufficient to combine with all the basic oxides except that which it is desired to reduce.

Fluxes are of three classes:

(1) **Acidic.** *Silica*, as quartz, sand, &c. *Natural silicates. Silicious slags.*

(2) **Basic.** *Lime* or *limestone* is the most important, being used in enormous quantities in iron smelting.

Dolomite or *magnesia* is useful also, but is more expensive.

Clay, *clay-slate*, &c., are largely used when the introduction of alumina is desirable.

(3) **Neutral.** *Fluor-spar.* This should be free from copper pyrites, blend, and galena, and, if possible, from quartz. Derbyshire spar is the best. It fluxes sulphates of calcium, lead, barium, calcium phosphate, silica, silicates, &c., with formation of a very fusible slag.

Roberts Austen (Metallurgy, 294) gives the following rules for the selection of fluxes to form a fusible silicate slag:—

If the gangue is silicious, two bases must be added, *e.g.* clay slate or argillaceous limestone.

If the gangue is argillaceous, the addition of one base, *e.g.* limestone, will suffice.

When the gangue is basic and contains two metallic oxides, the addition of quartz only is necessary, but when it contains only one base. clay, silicious slag, &c., must be added.

FORCITE *v.* EXPLOSIVES.

FORDIT. An explosive consisting of nitroglycerin (24·5), collodion cotton (1·0), nitrotoluene (34·0), flour (2·0), dextrin (2·0), glycerol (5·5), ammonium nitrate (32·0), and potassium chloride (30·0 parts).

FORGENIN. Trade name for tetramethyl ammonium formate.

FORMAL *v.* SYNTHETIC DRUGS.

FORMALDEHYDE (*formic aldehyde, formol, methanal*) CH_2O. Discovered in 1867 by A. W. Hofmann as a product of the flameless combustion of methyl alcohol. A red-hot coil of platinum wire suspended over methyl alcohol contained in a beaker, is kept red-hot so long as it is in contact with the mixture of air and methyl alcohol vapour, acting as a catalyst for the formation of the formaldehyde

$$CH_3OH+O=CH_2O+H_2O$$

Hofmann succeeded in isolating a small quantity of formaldehyde by passing the mixture of methyl alcohol vapour and air through a platinum tube heated to dull redness. Armand Gautier passed the methyl alcohol vapours through a horizontal tube heated in a sulphur bath.

Methods for preparing formaldehyde in larger quantities were devised by Tollens, Loew, and Kablukow. Air was bubbled through methyl alcohol at 40° to 50°, and the mixture of air and alcohol vapours passed over a spool of copper wire gauze 5 cm. long and moderately heated. The product was collected as an aqueous solution in a flask on a water-bath, and the gases and uncondensed vapours passed on to a receiver cooled by ice or water. Tollens found that the yield depended largely on the temperature of the methyl alcohol, and therefore on the degree of saturation of the air with alcohol:

Temp. of bath	Yield of CH_2O
22°–32°	17·95
38°–44°	28·90
45°–50°	31·15

Trillat proposed the first method for the production of formaldehyde on a manufacturing scale (Fr. Pat. 199919, 1889). His apparatus is shown in Fig. 1. Crude or rectified methyl alcohol is heated in the copper vessel A of about 100 litres capacity by passing steam through the bottom compartment *a*. The alcohol vapours are carried away by the copper pipe B fitted with a conical perforated mouthpiece C, and issue from the perforations in form of a fine spray. The mouthpiece penetrates a short distance into tube D of 10 cm. diameter and 1 m. length. Air can be aspirated through *x* at the conical end of D as indicated by the arrows. Platinised asbestos is placed in the widened part at E and heated by direct fire. Other contact substances which were suggested by Trillat are copper oxide, retort carbon, porcelain, coke, firebrick, and the like. The method of working is as follows:—

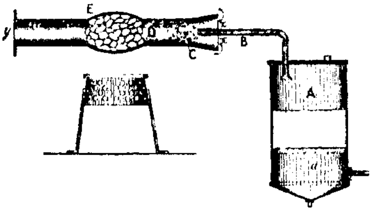


FIG. 1.

The tube is heated at E to a dull or bright red heat, according to the nature of the contact substance; the receiver, communicating with a vacuum pump, is then connected to *y*. The methyl alcohol is in the mean time brought to boiling-point; and the vapours produced, forming a spray, are mixed with air drawn in at *x*. The mixture reacts on meeting the contact substance, whereby the alcohol is oxidised to formaldehyde. The vapours contain water, undecomposed methyl alcohol, and traces of formic and acetic acids. The products are condensed or dissolved in water, and the solution is redistilled to drive off the impurities. Trillat gave no statement of yields, but these cannot have been very good, and his apparatus is therefore to-day only of historic interest. It formed, however, the basis for the present processes. Instead of boiling the alcohol and subsequently mixing its vapours with air, later processes drive or draw air through the methyl alcohol, kept at a temperature suitable for saturation, and pass the mixture over the contact substances.

M. Klar and C. Schulze proposed the introduction of the scrubber principle for this operation (Ger. Pat. 106495). They consider the large excess of alcohol over air obtained by the older method to be disadvantageous, and otherwise undesirable. At the same time, there is too little control over the ratio of the mixture. They therefore employ a scrubber, made of metal or stoneware, into which they pass a fine spray of wood spirit through a rose. Air, which has previously been heated high enough to obtain a mixture temperature of 45°–50°, is blown in at the bottom of the scrubber which may also be provided with a steam-jacket. By adjusting the flow of alcohol and air, the ratio of the mixture can be varied to any desired extent. In order further to moderate the oxidation, the air is diluted with a certain proportion of nitrogen obtained from the process itself, with the result that a smaller degree of saturation of the air is required. They claim advantages both in regard to the safety and the yield of their process. This process relates only to the preparation of the reacting mixture, but has no reference to the contact process proper.

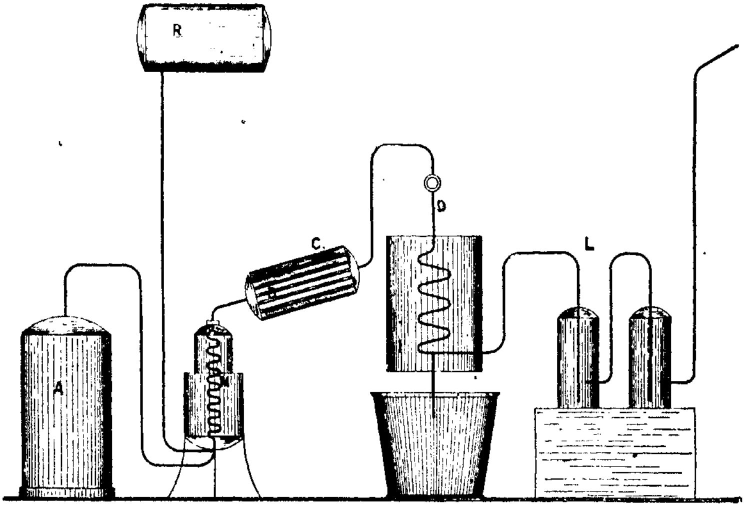


FIG. 2.

Fig. 2 shows the formaldehyde plant of a

French factory (Côte d'Or), as described by A. Morel (J. Pharm. Chim. 1905, 21, 177). The principal unit is the oxidiser, a metal cylinder C, fitted with copper tubes B in which the reaction takes place. Wood spirit is supplied from the tank R to the mixer M, constructed on the carburettor principle, and is here vapourised by, and in suitable proportions mixed with, air pressed in from reservoir A. The mixture reacts during its passage over copper contacts placed in the oxidiser tubes B kept at an elevated temperature. Sight holes permit of the observation of colour and luminosity, and consequently the temperature of the contact zone. The products are carried off through a single pipe, and are condensed in coil D surrounded by a current of water. The condensate, being crude formaldehyde solution, runs into a receiver. The uncondensed vapour is extracted from the gases in three washers, L. The crude product is freed from methyl alcohol in a rectifying still.

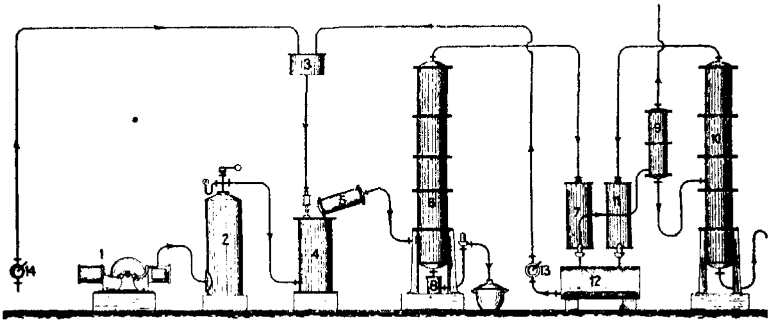


Fig. 3.

The modern plants for the manufacture of formaldehyde are built on the same lines, although greatly improved in some of the details, with the result of a greatly increased yield. In Fig. 3 a modern plant is shown. Compressor 1 aspirates air from the atmosphere and presses it into the air vessel 2, in which a constant pressure is kept. Methyl alcohol runs from tank 3 into the carburation vessel 4. A heating arrangement is placed in this apparatus which raises the temperature of the incoming air. This current of air meets a thin stream of methyl alcohol, which also takes up heat, and a mixture of constant composition is thereby formed. This enters the oxidiser 5, charged with the contact substance, which usually consists of copper gauze, but in some cases silver or silver-coated copper gauze is used in preference. The products of reaction issuing from the oxidiser, which consist of vapours of formaldehyde, water, and the excess of methyl alcohol, as well as nitrogen and hydrogen, pass into a separator. 6, in which, by a washing process, commercial formaldehyde (40 p.c. solution)—so-called 'formalin'—is obtained, which is drawn off into the receiver 8, whilst methyl alcohol vapours are almost completely condensed in 7, whence they run into reservoir 12, and are sent by pump 13 back into the feeding tank 3. The gases still contain some methyl alcohol, and are made to pass the washer 9 which extracts the last traces. This dilute alcohol is concentrated in the continuously working rectifying still 10. The concentrated alcohol vapours are again condensed in 11, and pumped back to 3.

J. E. Orloff has designed an apparatus which in many of its details is not unlike the above described. In Fig. 4 the 'carburettor,' A, consists of a vessel of 750 mm. diameter and 800 mm. height charged with methyl alcohol, to about one-half its capacity, from an overhead tank, B, and fitted with copper steam coils, *a*. Air is aspirated through the methyl alcohol by means of a perforated pipe. The air-alcohol mixture then passes a 'dephlegmator,' C, fitted with a steam coil, *c*, any excess alcohol being allowed to drain back into the carburettor. The mixture thus heated to the desired temperature enters the oxidiser. This consists of a tubular vessel set at an angle of about 10° and containing 169 copper tubes of 19 mm. internal diameter, 2 mm. thickness, and 800 mm. length, arranged in seven concentric circles between two plates of 820 mm. diameter, which are separated from the two cover plates by bronze rings of 720 mm. int. diam. A steam coil is placed in the ring on the inlet side to heat the mixture, which enters through a pipe 50 mm. wide. A number of sight holes are provided in the front plate, and a conical exit pipe is connected with the back ring. Glass tubes, 16 mm. wide, 1·25 mm. thick, and 300 mm. long, are placed in the copper tubes containing spools 120 mm. long, made of copper gauze. The gases after leaving the oxidiser are passed through a scrubbing column, E, 2000 mm. high from which the formaldehyde solution is run off through a water-cooled pipe, F. The gases are then led through a cooling coil, O, and a small scrubber, H, for the removal of methyl alcohol vapour. The condensate from the coil and the alcohol solution from the scrubber are collected in sump K, and pumped back into the feed tank. The gases leave the plant through a gas meter, M, and the exhauster. The air may be aspirated into the carburettor direct from the surrounding atmosphere or through the oxidiser drum, whereby it is preheated, and the catalyst incidentally cooled. In order to start the work of the oxidiser without the application of external heat, Orloff employs 'ignition pills,' made of platinised asbestos or pumice, close to the catalyst. These initiate the action at ordinary temperature when the alcohol vapours pass over them. When dispensing with external heating he found that alcohol vapour of 90 p.c. strength gives satisfactory results; this makes it possible to distil the alcohol completely without a rectifying column, whilst when working with a vapour of 100 p.c. strength the alcohol has to be rectified after a quarter has been distilled off. The dephlegmator is kept at 53°–54°, whilst 42°–43° is sufficient when 100 p.c. alcohol vapour is used. The methyl alcohol should not contain more than 1 p.c. acetone. The ratio of the volume of exit gases to the volume of air admitted should be 1·15 : 1 on an average. An apparatus of the size given oxidises 175 kgs. methyl alcohol in 10 hours, and the yield should be 150–155 p.c. by weight of the alcohol employed, the formaldehyde having a strength of 38–39 p.c.

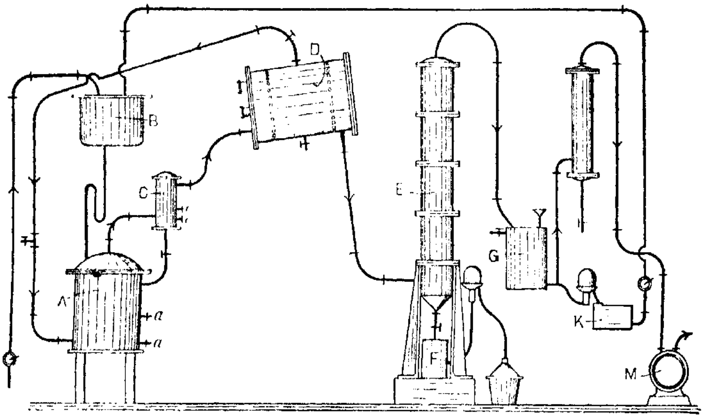


FIG. 4.

In G. C. Calvert's plant (Eng. Pat. 814, 1915), shown in Fig. 5, the carburettor consists of a rotary fan, A, of the annular blade type, encased in a steam-jacket. The methyl alcohol is run on the rotor through a sight feed. Air, which may be preheated by a steam coil, is taken in at *a*, and intimately mixed with alcohol in the fan. The mixture passes through an externally heated oxidiser, B, which is pierced with vertical flattened cooling tubes, through which water or steam may be circulated in order to keep down the temperature. The reaction gases then pass through a horizontal cooling chamber, C, fitted with a nest of cooling tubes, through which a current of air passes. The saturator, D, follows as an extension of the cooling chamber, and consists of a horizontal tube of the same diameter fitted with a shaft carrying vanes revolving at a high speed. Formaldehyde solution is fed into the saturator from feed-tank E, and discharges into the tank F, from which it is circulated by pump G, and periodically drawn off when it has reached the desired strength. The waste gases leave the apparatus at Z.

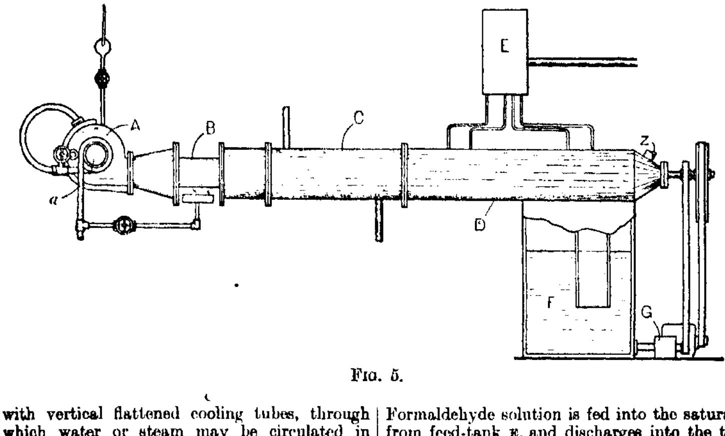


FIG. 5.

The bulk of the world's production of formaldehyde is made from methyl alcohol. There have, however, been various proposals for the employment of other raw products, for instance, methane or ethylene. The conversion of formates into formaldehyde by thermal decomposition has also been suggested, but no great success has been obtained with the industrial application of any of these methods (*see* Hofmann and Schibsted, Ber. 1918, 51. 1398).

W. A. Bone has shown that formaldehyde is formed as an intermediate product in the combustion of hydrocarbons, which he regards as a process of hydroxylation and scission of water molecules. The industrial application of partial combustion up to the stage of formaldehyde formation offers, therefore, a promising problem. Glock (Ger. Pat. 109014) suggests the oxidation of methane, or mixtures containing methane, by oxygen in the presence of copper, pumice or asbestos as a catalyst. Methane is mixed with an equal volume of air and passed through a tube filled with granulated copper heated to 600°. The products are cooled, washed with water, mixed with an equal volume of air, and again passed through a second tube with contact substance, and this process is repeated until all methane is oxidised. The first tube is kept hot by the reaction, the others require external heating. J. Gruszkiewicz proposes, in Austr. Pat. 46693, to burn methane, or natural gas rich in methane, with air insufficient for complete combustion, and to utilise the catalytic property of the soot, thereby produced, for effecting the oxidation to formaldehyde. The gases produced by the checked combustion are passed rapidly through a chamber fitted with baffle plates, for the removal of the soot, and are finally scrubbed with water, for the extraction of the formaldehyde produced. According to the inventor's claim, the carbon produced forms a valuable by-product. G. Fernekes, in U.S. Pats. 1038546 and 1038547, also proposes the production of formaldehyde from natural gas by partial combustion with air in baffled flames and cooling products.

The Verein f. chem. Ind. (Ger. Pat. 286731) employs a gas mixture consisting of about 3 parts methane and 100 parts moist air, and conducts this mixture in a closed system over a contact substance such as copper or silver, or both, at a temperature of 150°-200°, when a portion of the methane is converted into formaldehyde.

Since acetaldehyde is produced from acetylene with mercury as catalyst, it is possible that wet methods carried out on similar lines may give better results in the formation of formaldehyde than direct atmospheric combustion. Hydrogen peroxide, or, according to Lange and Elworthy's Fr. Pat. 352687, electrolytically produced persulphuric acid, have been suggested as oxidising agents in the production of formaldehyde from alcohol.

Theory of the catalytic process. After the early work of Hofmann, Tollens, Loew, Kablukow, the subject was closely investigated by Trillat, who published these researches in his book 'Oxydation des Alcools par l'action de contact.'

He studied the influence of varying temperatures, proportion of air and of water, and of different contact substances, on the oxidation process. His conclusions were partly incorrect, particularly with regard to the proportion of water vapour to methyl alcohol, which he, in contradistinction to other investigators, did not consider injurious.

J. E. Orloff, in a series of papers in the Journal of the Russian Chemical Society (see also his 'Formaldehyd,' Leipsic, 1909), assumed the main reaction to be:

$$2CH_3OH + O_2 = 2CH_2O + 2H_2O$$

with a secondary oxidation to formic acid and carbon dioxide, and carbon monoxide and water. No traces of formic acid could, however, be found, but always hydrogen, and he therefore suggested a partial decomposition:

$$CH_2O = CO + H_2$$
$$CO + O = CO_2$$
$$H_2 + O = H_2O$$

The main reaction is not in accordance with the facts established by Ipatieff and by Sabatier and Senderens, who had proved the catalytic decomposition of alcohols into aldehydes and hydrogen generally, with copper as catalyst. M. Le Blanc and E. Plaschke (Zeitsch. Elektrochem. 1911, 17, 45) have established that the formation of formaldehyde is due not to oxidation, but to catalytic dehydrogenation of methyl alcohol. The activity of freshly reduced copper or silver decreases rapidly unless air is introduced with consequent temporary oxidation of the metal. This is again reduced at the expense of alcohol and possibly aldehyde. An undesirable secondary reaction is the decomposition of formaldehyde into hydrogen and carbon monoxide. The yield is dependent upon the temperature of the contact body, the ratio of alcohol to air or oxygen, and the surface of the contact body. The highest yield was 58 p.c., and the lowest loss of destroyed alcohol 12 p.c.

M. D. Thomas (J. Am. Chem. Soc. 1920, 42, 867) confirms Le Blanc and Plaschke's work, but obtained rather higher yields. The absolute yields with silver, copper, and gold were 95·0 p.c., 90·5 p.c., and 88·5 respectively, corresponding to process yields of 55·6 p.c., 50·5 p.c., and 40 p.c. A reaction mixture containing 0·4 to 0·5 gram of oxygen per gram of alcohol gave the best results with silver, whilst copper required 0·55 to 0·65 gram of oxygen.

Catalysts.—In the early attempts to produce formaldehyde, platinum wire, platinum sponge, or platinised asbestos were mostly employed as catalytic bodies, and these are still used in the familiar type of formaldehyde lamp for disinfecting rooms (*e.g.* Schlichter, Eng. Pat. 401, 1887).

In most of the industrial plants copper, in the form of fine wire gauze, has been employed until recently. A number of other catalysts, such as copper filings, copper-coated asbestos, fire-brick, coke or charcoal, vanadium oxide, silver, and metals of the platinum group have been proposed from time to time. S. Fokin (J. Russ. Phys. Chem. Soc. 1913, 45, 286) studied the effect of different catalysts on mixtures of methyl alcohol vapour and air, and found their activity to be in the following order: Co 2·8, Ni 1·08, Al 1·5, Mn 2·01, Pt 5·2, Cu 43–47, Ag 64–66, Au 71, and Cu+Ag 84 p.c. of the theory. In other comparative experiments Fokin found the order of efficiency to be Au<Cu<Ag, and he assumes as probable the formation of labile oxides.

On the other hand, Le Blanc and Plaschke (*l.c.*) found in their researches that the catalytic effect of silver was not appreciably superior to that of copper. In a number of patents, however, a greatly improved efficiency is claimed for silver as catalyst (Blank, Ger. Pat. 228697; Kusnezow, U.S. Pat. 1067665; Bouhard, Fr. Pat. 412501; H. von Hochstetter and Holzverkohlungs, Ind. A. G. Eng. Pat. 464, 1914; U.S. Pats. 1100076 and 1110289), who employ as catalyst metal couples particularly of metals of the platinum group and silver claim for these highly increased yields. These couples must not be in the form of alloys, but in mechanical combination. In effect, this arrangement has been used in all cases where several metals have entered into the construction of a formaldehyde lamp or oxidiser using a platinum catalyst.

Yields.—The yield of formaldehyde from a given quantity of methyl alcohol may vary within very wide limits and never reaches the theoretical value of the equation

$$CH_3OH+O=CH_2O+H_2O$$

The yield depends on the purity of the methyl alcohol and air, the ratio of the mixture, the catalyst employed, its surface, temperature, and length, the velocity of the gases over it and, therefore, the time-contact, the rapidity of cooling of the gases, and, finally, the completeness of extraction of formaldehyde and methyl alcohol vapour from the exit gases. The actual loss is caused by decomposition of alcohol into CO_2, CO, and H_2O. A certain amount of methyl alcohol must pass through the system undecomposed. A portion of this is left in the final product, whilst the balance can be recovered almost completely in an efficient plant. A yield of 150–160 parts 40 p.c. formaldehyde solution from 100 parts methyl alcohol may be regarded as normal, although yields up to 175 p.c. have been obtained from specially purified alcohol and under particularly favourable conditions of supervision and working The apparent increase in weight is due to the addition of water as the solvent.

The '40 p.c. formaldehyde' of commerce contains 40 grams per 100 c.c. and has, therefore, a true strength of only 36 p.c. It is in fact usually weaker. The article required by the British Pharmacopœia contains not less than 36, and not more than 38 grams CH_2O per 100 c.c. and has a specific gravity of 1·080.

On keeping, formaldehyde is converted by polymerisation into diformaldehyde and trioxymethylene, causing cloudiness and deposits in solution. To prevent this a certain percentage of methyl alcohol is left in the product, which may, for instance, have the following composition: 36 p.c. formaldehyde, 12 p.c. methyl alcohol, 52 p.c. water.

Formaldehyde is a gas of characteristic smell which, on cooling, condenses to a liquid of b.p. −21° and of sp.gr. 0·8153 at −20° or 0·9172 at −80°. Liquid formaldehyde changes at −20° readily into a solid modification; the melting-point of monomolecular CH_2O is −92°. Water absorbs up to 52 p.c. formaldehyde; the freshly prepared concentrated solution, which has a pungent smell and strong irritant action on the mucous membranes, contains diformaldehyde or methyleneglycol $CH_2(OH)_2$, which changes into formaldehyde on standing. Dilute solutions contain the monomolecular form CH_2O, and do not undergo any change when kept in closed vessels. But on concentrating the solution in a desiccator or by evaporation, polymerisation takes place, flocculent masses of $(CH_2O)_nH_2O$ (n =6 to 8) being precipitated, which form the commercial paraformaldehyde.

The specific gravity of commercial formaldehyde solutions freed from methyl alcohol were determined by W. A. Davis (J. Soc. Chem. Ind. 1897, 16, 502).

Spec. grav. at 60° F.	P.c. CH_2O by weight	Grams CH_2O per 100 c.c.
1·005	2	2·0
1·010	4	4·0
1·015	6	6·1
1·020	8	8·2
1·025	10	10·25
1·030	12	12·4
1·038	15	15·6
1·053	20	21·1
1·064	24	25·5
1·076	28	30·1
1·083	30	32·5
1·087	31	33·7
1·092	32	34·9
1·096	33	36·2
1·100	34	37·4
1·104	35	38·6
1·109	36	39·9
1·113	37	41·2
1·117	38	42·5
1·121	39	43·7
1·125	40	45·0

The aqueous solution precipitates from an ammoniacal silver solution a specular deposit of silver, and, on treatment with hydrogen sulphide, yields crystals of trithiomethylene $(CH_2S)_3$ (Hofmann, Annalen, 145, 360). On heating formaldehyde with a dilute solution of sodium hydroxide, formic acid and methyl alcohol are produced. With concentrated sodium hydroxide solution and a little Cu_2O, formic acid is produced at ordinary temperature, accompanied by violent evolution of hydrogen (Loew). Formaldehyde readily combines with ammonia to form the monacid base *hexamethylenetetramine*, according to the equation:

$$6CH_2O+4NH_3=N_4(CH_2)_6+6H_2O.$$

As this reaction takes place even in dilute solution, it forms a convenient method for the titrimetric determination of formaldehyde (Butlerow, Annalen, 115, 322; Legler, Ber. 16, 1333; Loew, J. pr. Chem. 1886, 33, 326). It crystallises from alcohol in rhombohedra, is very soluble in water and alcohol, and insoluble in ether.

Formaldehyde condenses with aniline with loss of water to *anhydroformaldehydeaniline*

$$CH_2O+C_6H_5NH_2=C_6H_5N:CH_2+H_2O$$

On heating formaldehyde with a solution of ammonium sulphate, *trimethylamine sulphate* is formed, whereby one-third is oxidised to CO_2 (Plöchl, Ber. 21, 2117). $CH_2O,NaHSO_3,H_2O$ is formed by adding $NaHSO_3$ and alcohol to formaldehyde solution; this is readily soluble in water and methyl alcohol, less soluble in ethyl alcohol. By the action of hydrogen chloride on formaldehyde, Tischtschenko obtained *dichloromethyl ether* and water. Lösekann obtained, by the same treatment, *oxychloromethyl ether*, which further yielded *monochloromethyl alcohol* (Ber. 25, 92). By careful treatment with bases such as calcium hydroxide or lead oxide, formaldehyde may be polymerised into a mixture of saccharine substances. By continued boiling of such a solution with tin, *iso*formose is obtained; treatment with lime water yields *a-acrose* $C_6H_{12}O_6$.

If formaldehyde solution is concentrated in the presence of dehydrating agents, it polymerises to *trioxymethylene* $(CH_2O)_3$, a crystalline mass fusing at 171°–172°, but subliming below 100°; insoluble in water, alcohol, or ether at ordinary temperature, but soluble in water when heated to 130°, when it appears to be converted into formaldehyde or paraformaldehyde (Tollens and Mayer, Ber. 21, 3504). When trioxymethylene is volatilised, it dissociates completely into formaldehyde (v.d. 15·3, Hofmann). When boiled with lime water, it yields formic acid and an amorphous saccharine substance, *methylenitan* (Butlerow, Annalen, 120, 295).

When dry trioxymethylene is heated in a sealed tube with traces of sulphuric acid at 115°, it is converted into the isomeric α-trioxymethylene $(CH_2O)_3$, which crystallises in needles, melts at 60°–61°, and sublimes at ordinary temperature, and is soluble in water, alcohol, and ether (Pratesi, Gazz. chim. ital. 14, 139).

Auerbach and Barschall (Arb. Kais. Gesundh. Amt. 27, part 1) claim to have established the identity of six individual polymerides: paraformaldehyde $(CH_2O)_n+H_2O$, four polyoxymethylenes $(CH_2O)_n$ and α-trioxymethylene $(C_3H_6O_3)$ of ring structure, characterised by their form (amorphous, colloidal, indefinite crystals, definite crystals, and well-developed crystals), melting-point, solubility, &c.

Formaldehyde is capable of reacting with practically any class of organic, and a large number of inorganic, substances, and forms numerous condensation products. It reacts with hydrocarbons, carbohydrates, aldehydes, and ketones, carboxylic, oxy- and keto- acids and their esters, phenols, oxyaldehydes, gallic and tannic acid, amines, ammonia, hydrocyanic acid, hydrazines, hydroxylamine, urea, uric acid, guanidine, the proteins, nitro compounds, quinoline, pyridine, and sulphur compounds.

Its formation plays an important part in the assimilation of carbon dioxide by chlorophyll-containing plants (Baeyer, Bach, Loeb, Délépine). For the synthesis of formaldehyde and carbohydrates from carbon dioxide and water by photocatalysis, *see* Baly, Heilbron, and Barker, Chem. Soc. Trans. 1921, 119, 1025).

Atraclylis gummifera contains an active glucosidal principle, *atractilin*, which with 2 or 3 drops of concentrated sulphuric acid gives a yellow coloration, changing to violet and bright blue if treated with a trace of formaldehyde. By means of this reaction the presence of formaldehyde in the juices of green leaves, when exposed normally to light, may be detected; formaldehyde is absent from the juices of the leaves of the same plants after being kept 24 hours in the dark (Angelico and Catalano, Gazz. chim. ital. 1913, 43, 38; Analyst, 1913, 152).

The industrial employment of formaldehyde is manifold, in keeping with its enormous reactivity. The coal-tar colour industry uses it very largely for condensation products; a great number of pharmaceutical preparations have formaldehyde as their active principle. In most of these, use is made of its antiseptic powers by condensation with a variety of drugs.

The antiseptic properties of formaldehyde are essentially due to its chemically combining with the cell skin of the micro-organisms, thereby hardening it and inhibiting their growth. It is employed in a number of ways and in different combinations. It is used in the treatment of wounds and for sterilising surgical instruments and the hands of operators, occasionally compounded with soap, as in *lysoform*. For disinfecting rooms a 1 or 2 p.c. solution of formaldehyde may be used as spray, and is non-injurious to coloured fabrics. A concentrated solution or solid paraformaldehyde may be vaporised in a lamp, and its diffusive and penetrating qualities make it applicable where other disinfectants cannot be employed. The best known forms of apparatus for this purpose were devised by Trillat, Tollens, Krell, Barthel, and Schering. In certain cases, as for instance in the treatment of frozen meat on board ship, an air current is passed through a vessel containing formaldehyde solution heated by steam coils. It has also been proposed to treat a mixture of paraformaldehyde and peroxides of the alkaline earths with water, when a violent liberation of formaldehyde vapour takes place (Autan). Permanganate, or other oxidising agents, are similarly used with paraformaldehyde.

Its preservative qualities are made use of in embalming and for the preservation of corpses for dissection. It is largely used for the preserving of foodstuffs, and possibly the effect of 'curing' is in a measure due to the formaldehyde produced from burning wood and other carbonaceous materials.

Formaldehyde is employed in the brewing, distilling, and sugar industries, and besides its preservative action, a certain stimulative effect on the diastatic properties of the malt, and on the activity of yeast, has been observed. Formaldehyde is largely used for tanning purposes, especially for sole leather. By its action on proteid bodies, it makes the leather hard and firm without having the bad effect of acids. Formaldehyde solution is also used for coagulating rubber latex; and the result of curing para rubber over wood fires has been ascribed, at least in part, to the presence of formaldehyde vapour. In the paper-making and textile industries, it is used for fixing glues and sizes, and also for water-proofing fabrics, by rendering gelatin or casein insoluble. Upon the same reaction is based its employment in hardening the gelatin films of photographic plates, and for hardening microscopic preparations and anatomical museum specimens.

Formaldehyde is also used as a reducing agent in the recovery of silver and gold, and in the preparation of metallic mirrors. A material for the manufacture of bone-like articles is made by the action of formaldehyde on caseinogenate (galalith). The water-proofing of straw hats is effected by impregnating them with a solution of gelatine which is then hardened with formaldehyde. On the condensing reaction of formaldehyde with phenol or cresols is based the manufacture of a substitute for horn, tortoiseshell, &c. The best known of these condensation products is 'bakelite,' which is used in solution as a lacquer or varnish, or, in its solid form after being subjected to high pressure, for electrical insulation purposes (*v.* BAKELITE).

The action of dry gaseous hydrogen chloride in the cold on commercial formaldehyde solution (about 40 p.c.) in a reflux apparatus yields, first, the compound $OH{\cdot}CH_2Cl$. If the action is prolonged, a heavy liquid $O(CH_2Cl)_2$ separates. This liquid, treated with a mixture of concentrated nitric and sulphuric acids at 5°, forms a colourless oil of sp. gr. 1·522, of the composition $C_2H_4O_6N_2$, or $NO_2{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}O{\cdot}NO_2$, which on hydrolysis yields formic acid and nitromethane. It is extremely sensitive to shock and decomposes with detonation. It dissolves considerable amounts of cellulose nitrate and an explosive jelly containing 7 p.c. of cellulose nitrate (12·11 p.c. N) gives a greater increase in volume on explosion than one containing 7 p.c. of glyceryl nitrate (Moreschi, Atti. R. Accad. Lincei, 1919, [v.] 28, i. 277).

For the qualitative detection of formaldehyde, a number of reactions have been proposed, most of which are based on colour reactions. On warming with ammoniacal silver solution, the silver mirror is produced. Schiff's reagent is frequently used; 0·4 gram magenta is dissolved in 25 c.c. of water; 10 c.c. of sodium bisulphite solution (sp.gr. 1·375), and then 10 c.c. of strong sulphuric acid are added; formaldehyde causes a red coloration which, on addition of hydrochloric acid, changes to bluish violet. Other reagents suggested are alkaline resorcinol, phloroglucin, codeine, morphine, phenyl hydrazine, and ferric chloride.

For the quantitative determination, the following are used: Legler's method based on the reaction of ammonia on formaldehyde, gives low results. For impure concentrated solution, the method of Blank and Finkenbeiner (Ber. 31, 2979) may be employed. It consists in oxidising formaldehyde to formic acid by means of hydrogen peroxide in alkaline solution. An iodometric method was suggested by Romijn (Zeitsch. anal. Chem. 36, 19), and many colorimetric reactions have been worked out for the exact estimation of small quantities of formaldehyde. 1 part of formalin in 100,000 parts of milk can be detected by distillation and application of colour reactions to the distillate. Rideal and Hehner have studied the rate of disappearance of formalin when added to milk by formation of condensation products. Schryver uses phenyl hydrazine and potassium ferricyanide for the estimation of formaldehyde in a dilution of 1 : 1,000,000. R. L.

FORMALIN. A 40 p.c. solution of formaldehyde.

FORMAMIDE $HCO{\cdot}NH_2$. First obtained by Hofmann (J. pr. Chem. 91, 61) by heating ethyl formate with ammonia in a sealed tube at 100°.

It is a product of the oxidation of amino-acids, lactic acid, albumin, &c., by ammoniacal potassium permanganate (Hasley, Zeitsch. physiol. Chem. 25, 325).

It is formed by the action of the silent discharge on a mixture of carbonic oxide and ammonia (Losanitsch and Jovitschitsch, Ber. 30, 138); by distilling sodium formate with ammonium chloride in a vacuum (Verley, Bull. Soc. chim. 9, [3] 691); or by heating crystallised ammonium formate in a sealed tube at 230° for 5 hours (Hofmann, Ber. 15, 980), but is best prepared by heating pure dry ammonium formate for 2 hours at 100°–180° in an atmosphere of ammonia, then fractionating in the same atmosphere at ½ mm. pressure (Freer and Sherman, Amer. Chem. J. 20, 223).

Formamide is a liquid, b.p. 85°–95° (½ mm. pressure); at ordinary pressure it decomposes, when heated above 100°, into carbon monoxide, ammonia, hydrogen cyanide, and water. It crystallises in needles, m.p. 2·25° (Brann); sp.gr. 1·76 at 4° (Freer and Sherman, *l.c.*). Phosphoric pentoxide converts it into water and hydrocyanic acid: $HCO{\cdot}NH_2 = HCN + H_2O$. Strong caustic potash decomposes it, even in the cold, into potassium formate and ammonia. It is also decomposed by a mixture of potassium chromate and sulphuric acid, forming carbon dioxide and ammonium hydrogen sulphate; by hydrogen peroxide with production of ammonia and carbon dioxide (de Coninck, Compt. rend. 128, 503); and by sodium hypochlorite on heating (de Coninck, *ibid.* 121, 893). Formamide combines with chloral forming chloral-amid or *chloralum formamidatum*, used as a disinfectant and as a preservative, and for its hypnotic properties (*v.* CHLORAL). Sodium, silver (Freer and Sherman, Amer. Chem. J. 562 and *l.c.*; Titherley, Chem. Soc. Trans. 1897, 466) and mercury salts have been obtained (Fischer and Grützner, Arch. Pharm. 232, 329). Condensation products of value as antiseptics and solvents for uric acid are obtained by condensing formamide with formaldehyde, paraldehyde, or trioxymethylene (J. Soc. Chem. Ind. 25, 283).

FORMAMIDINE, *Methenylamidine*

$$CH(NH)(NH_2).$$

This compound, the lowest member of the amidine series, may be regarded as formamide $HCO{\cdot}NH_2$ in which the oxygen atom has been replaced by imidogen. Obtained by acting on the double compound of hydrocyanic acid and hydrochloric acid with absolute alcohol:

$$2HCN,HCl+2C_2H_5{\cdot}OH$$
$$=CH(NH)(NH_2),HCl+C_2H_5Cl+HCO_2{\cdot}C_2H_5$$

(Gautier, Compt. rend. 65, 410; *cf.* Claisen and Matthews, Chem. Soc. Trans. 1882, 265). From the hydrochloride of formimido-ether

$$CH(NH)(OC_2H_5),HCl$$

and alcoholic ammonia (Pinner, Ber. 16, 375, 1647). Formamidine hydrochloride crystallises from alcohol in hygroscopic granules, melting at 81°, and decomposing at 100° into hydrocyanic acid and ammonium chloride:

$$CH(NH)(NH_2)HCl=HCN+NH_4Cl.$$

When liberated from its salts by caustic potash, formamidine is at once decomposed into ammonia and potassium formate. Its salts crystallise with difficulty. $(CH_4N_2,HCl)_2,PtCl_4$ forms very soluble, orange-red, quadratic pyramids.

Formamidine picrate

$NH : CH{\cdot}NH_2,C_6H_2(NO_2)_3OH$

obtained by the addition of formamidine hydrochloride to picric acid, crystallises in long lustrous yellow needles, m.p. 248° (Dieckmann, Ber. 25, 705).

Substitution derivatives of formamidine have been studied by Dains (*ibid.* 35, 2496).

FORMAMINT. Trade name for a preparation of lactose and formaldehyde.

FORMAN. Trade name for chlormethylmenthyl ether $C_{10}H_{19}{\cdot}O{\cdot}CH_2Cl$, formed by the action of formaldehyde upon menthol in the presence of hydrochloric acid. A colourless, fuming oil, b.p. 160°–162°, 16 mm. pressure, decomposed by water into its original constituents. Employed in medicine in catarrhous affections of the air passages (*v.* SYNTHETIC DRUGS).

FORMANILIDE $HCO{\cdot}NH{\cdot}C_6H_5$, or

$OH{\cdot}CH : N{\cdot}C_6H_5$

(Claisen, Annalen, 287, 360: Wheeler and Medcalfe, Amer. Chem. J. 19, 217). First obtained by Gerhardt (Annalen, 60, 310) by heating aniline oxalate. Best prepared by heating together molecular proportions of aniline and strong formic acid on the water-bath under reduced pressure to remove the water, then distilling under ordinary pressure until the thermometer indicates 250°, and finally pouring out the undistilled portion, when it solidifies on standing (Wallach and Wüsten, Ber. 16, 145).—Long four-sided prisms melting at 46°, moderately soluble in water, readily so in alcohol. Dilute acids decompose it into aniline and formic acid. Formanilide is rapidly attacked by chromic acid, various colouring matters being formed (de Coninck, Compt. rend. 128, 503).

Sodium, silver (Comstock, Ber. 23, 2274; Comstock and Kleeberg, Amer. Chem. J. 12, 493), and mercury compounds have been obtained (Wheeler and McFarland, *ibid* 18, 540).

Other derivatives are described by Comstock and Kleeberg (*l.c.*), Claisen (*l.c.*), and Comstock and Wheeler (Amer. Chem. J. 13, 514).

FORMATOL. Trade name for a preparation of formaldehyde. Used as an antiseptic.

FORMESTON. Trade name for basic aluminium formate. Used in wound dressing.

FORMIC ACID (Ger. *Ameisensaure*) H·COOH. Discovered by Rey, in 1670, by distilling red ants with water. Formed in the acid secretions of certain caterpillars; in the common nettle (*cf.* Dobbin, Proc. Roy. Soc. Edin. 1919, 39, 137); in the fruit of the soap-nut tree (*Sapindus saponaria* (Linn.)); in tamarinds, &c. Occurs in sweat, urine, and muscular plasma. Formed by the dry distillation of starch, sugar, gum, tartaric and oxalic acids, &c. It may be prepared from acetylene by dissolving in fuming sulphuric acid and diluting with water. On boiling with baryta and filtering, the soluble barium formate remains in the filtrate. Best obtained in the laboratory by heating a mixture of glycerol (or other polyatomic alcohol of high boiling-point) with crystallised oxalic acid. The anhydrous glycerol is heated with the oxalic acid to 75°–90° until the evolution of carbon dioxide ceases, when a fresh quantity of oxalic acid is added, and the process repeated.

The interpretation of this reaction usually accepted is that the oxalic acid $C_2H_2O_4,2H_2O$ decomposes into water, carbon dioxide, and formic acid, which reacts upon the glycerol, forming *monoformin.* On the addition of a further quantity of crystallised oxalic acid, the water of crystallisation decomposes the monoformin, producing glycerol and formic acid, which distils over

$$\underset{\text{Glycerol.}}{C_3H_5(OH)_3}+\underset{\text{Formic acid.}}{H{\cdot}COOH}=\underset{\text{Monoformin.}}{HCO{\cdot}OC_3H_5(OH)_2}+H_2O$$

Monoformin is thus being continually formed and destroyed, with the eventual production of formic acid of from 87 to 88 p.c. (Lorin, Bull. Soc. chim. [ii.] 5, 7; 20, 241; 24, 22 and 436).

According to Chattaway (Trans. Chem. Soc. 1914, 151), glyceryl oxalate and glyceryl acid oxalate are the first products of the reaction. The latter is unstable at a slightly higher temperature, and decomposes, giving carbon dioxide and monoformin. The further addition of acid displaces formic acid from the monoformin.

The formates (*see* below) are the starting-point for the manufacture of formic acid. Whereas, at one time, oxalic acid was the source from which formic acid was obtained, now formates can be used as a source of oxalic acid (D. R. P. 111078, 144150, 161512). Formic acid is obtained by heating formates *in vacuô* with acids or acid salts (Hempel, Eng. Pat. 3428; J. Soc. Chem. Ind. 1909, 259): by treating formates with hydrofluoric acid (Strauss, D. R. P. 209418; J. Soc. Chem. Ind. 1909, 674); and by heating in a still 1 part of sodium formate with 2 parts of sodium hydrogen sulphate or other acid salt; in the last method, acid of from 97 to 98 p.c. is obtained (Ch. Fab. Grünaw, Landshoff, und Meyer, Akt. Ges., Eng. Pat. 14438; D. R. P. 192881; Fr. Pat. 367316; U.S. Pat. 857046; *v.* also Hamel, Eng. Pat. 7534; Fr. Pat. 341764; U.S. Pat. 806660; J. Soc. Chem. Ind. 1904, 9113, and Soc. Anon. des Etab. Eycken and Leroy; Fr. Pat. 393526; J. Soc. Chem. Ind. 1909, 160).

Anhydrous formic acid may be obtained by gently heating lead formate with sulphuretted hydrogen, by heating the dehydrated sodium salt with anhydrous oxalic acid, by distilling the ordinary acid over anhydrous copper sulphate under a pressure of 120 mm., or by the careful addition of phosphoric oxide and subsequent distillation under 15–18 mm. pressure (Jones, J. Soc. Chem. Ind. 1919, 38, 362 T.). It is a colourless, slightly fuming liquid, with a penetrating smell, and is intensely corrosive. Boils at 99·9°, sp.gr. 1·226 at 15°, 1·2200 at 20°; b.p. 101° (corr.) (Thorpe and Rodger); solidifies at a low temperature, forming large brilliant plates; m.p. 8·35°. Traces of water lower the m.p. and raise the b.p. The specific gravity of aqueous solutions is given in the following table (Richardson and Allaire, Amer. Chem. J. 19, 150):—

P.c.	Sp.gr. 20°/4°	P.c.	Sp.gr. 20°/4°
10	1·0247	60	1·1425
20	1·0489	70	1·1656
30	1·0730	80	1·186
40	1·0964	90	1·204
50	1·1208	—	—

Formic acid is readily decomposed catalytically according to one or more of the following equations : (1) $HCOOH=CO_2+H_2$;
(2) $HCOOH=CO+H_2O$;
(3) $2HCOOH=HCOH+CO_2+H_2O$.

By leading the vapour over the following heated substances it is decomposed in accordance with equation (1) at varying rates and temperatures: palladium, platinum, copper, nickel, cadmium and oxides of zinc and tin. Palladium sponge and platinum sponge bring about total decomposition at 245° and 215° respectively. Titanic oxide and the blue oxide of tungsten decompose the acid according to equation (2): Silica, zirconia, alumina, and uranous oxide in addition to carbon monoxide and water produce formaldehyde. With thoria all three reactions are possible, depending upon the temperature. A heated Jena glass tube at 340° decomposes the acid into carbon dioxide and hydrogen. Powdered pumice, magnesia, and wood charcoal resolve it into carbon monoxide and water (Sabatier and Mailhe, Compt. rend. 1911, 152, 1212).

Heated with concentrated sulphuric acid, formates evolve carbon monoxide; with ferric chloride neutral solutions give a red colour. Silver nitrate is reduced to metallic silver, which is precipitated, partly as a black powder, and partly as a lustrous deposit on the tube. Mercuric chloride is reduced to mercurous chloride, and if excess of formic acid is present, to metallic mercury.

Formic acid may be estimated by the method of Jones (Amer. Chem. J. 17, 539). The solution is made alkaline with sodium carbonate, warmed, and an excess of standard permanganate added. The solution is acidified, and a measured volume of oxalic acid is run in, until the precipitate of manganese hydroxide has dissolved and the permanganate disappeared. The excess of oxalic acid is estimated by titration with standard permanganate. A volume of oxalic acid equal to that taken is also titrated with permanganate solution, and the difference between the result and the total permanganate used gives the quantity of permanganate required to oxidise the formic acid (*v.* also Rupp, Zeitsch. anal. Chem 1906, 687; Grossmann and Aufrecht, Ber. 1906, 2455). Other methods depend on the reduction of mercuric chloride to mercurous chloride (Scala, J. anal. and appl. Chem. 5, 233; Lieben, Monatsh. 1893, 746; Leys, Mon. Sci. 12, 632; Franzen and Greve, J. pr. Chem. 1909, 80, 368; Riesser, Zeitsch. physiol. Chem. 1915, 96, 355); the titration of the acid with standard alkali, or the decomposition of the acid in the carbonic acid apparatus with sulphuric acid and potassium dichromate (Rupp, Arch. Pharm. 243, 69). For estimation in the presence of acetic acid, *v.* Freyer, Chem. Zeit. 1895, 1184; Heuser, *ibid.* 1915, 57; Laufmann, *ibid.* 1915, 575. In presence of other substances, *v.* Fincke, Biochem, Zeitsch. 1913, 50, 253; Analyst, 1913, 378.

Formic acid is a strong reducing agent and a powerful antiseptic. It is used as a food preservative (Woodman and Burrell, Tech. Quart. 1908, 21, 1), and in brewing is added to the yeast mash as an antiseptic (Lange, J. Soc. Chem. Ind. 1905, 1025; Henneberg, *ibid.* 1906, 192). It is used in dyeing as an assistant or reducing agent with potassium dichromate mordant and also for dyeing woollen goods or unions with acid dyestuffs (Kapf, *ibid.* 1905, 129; Meltner, *ibid.* 435; and Ruby, *ibid.* 1907, 467).

The formates.—Industrial methods for the preparation of the formates are based on three reactions: (1) The interaction of carbon monoxide and metallic oxides. In this method, carbon monoxide under pressure is passed over metallic oxides, basic minerals, or alkali hydroxides, the conditions varying slightly in the different processes (Usines des Moulins, Fr. Pat. 382001; J. Soc. Chem. Ind. 1908, 183; Ellis, U.S. Pat. 875055, *ibid.*; Raschen, J. Soc. Chem. Ind. 1908, 420; Eng. Pat. 13953; Farb. Meister, Lucius, and Bruning, Fr. Pat. 389065; J. Soc. Chem. Ind. 1908, 769; Haase, Eng. Pat. 4771; J. Soc. Chem. Ind. 1908, 898; Elect. Werke, D. R. P. 179515; Chem. Soc. Abstr. 1907, [i.] 378; Koepp and Co. D. R. P. 209417; Fr. Pat. 342168; Chem. Zentr. 1909, [i.] 1785). (2) The hydrolysis of the cyanides of the alkaline earth metals. The cyanides of the alkaline earth metals are treated with water vapour under pressure at temperatures below 300°, whereby ammonia and a formate are produced (Bad. Anil. und Soda Fab., Eng. Pat. 22038; Fr. Pat. 372714; J. Soc. Chem. Ind. 1907, 527; Eng. Pats. 784, 1912; 11485, 11486, 1915). The interaction of a solution of potassium ferrocyanide with caustic potash according to the following equation has also been patented by Haakh (D. R. P. 281044):

$$K_4Fe(CN)_6+14H_2O$$
$$=4HCOOK+2HCOONH_4+4NH_3+Fe(OH)_2.$$

(3) The reduction of carbonic acid or the carbonates by hydrogen. Rogation (Eng. Pat. 12604; J. Soc. Chem. Ind. 1893, 864) obtained a mixture of ammonium formate and bicarbonate by passing moist nitrogen, hydrogen, and carbon dioxide over slightly heated pumice or other absorbent bodies. Water gas and 'Ebelmen gas' were used to supply the hydrogen and nitrogen respectively. More recently the reduction of carbonic acid and the bicarbonates by hydrogen under pressure has been studied by Bredig and Carter (Ber. 1914, 541). They showed that calcium carbonate heated with hydrogen under 50 atmospheres pressure and carbon dioxide (20 atmospheres) at 70° in the presence of spongy palladium in 4½ hours gave a 100 p.c. yield of calcium formate. A 75 p.c. yield of potassium formate was obtained by passing hydrogen at 60 atmospheres pressure through a 5 p.c. solution of potassium bicarbonate containing palladium black (Eng. Pats. 801 and 9762, 1915).

Decomposition of the formates.—The formates of the alkali metals on heating in absence of air to 400° decompose, giving mainly hydrogen and oxalic acid, at lower temperatures carbonates are chiefly formed. The formates of the alkaline earths give only carbonates. The presence of two molecular proportions of calcium hydroxide lowers the temperature of decomposition of calcium formate from 375° to 260°, the proportion of hydrogen rising from 35 to 93 p.c. (Levi and Piva, Ann. Chim. Applicata, 1916, 271). Under certain conditions formaldehyde is one of the products of the reaction (Hofmann and Schumpelt, Ber. 1916, 303).

Potassium formate **HCO_2K and *Sodium formate* HCO_2Na are readily soluble deliquescent salts which, according to Bineau, form acid salts on solution in hot concentrated formic acid.** ***Calcium formate*** $(HCO_2)_2Ca$ and *Barium formate* $(HCO_2)_2Ba$ crystallise in rhombic prisms, readily soluble in water, insoluble in alcohol. *Lead formate* $(HCO_2)_2Pb$ is less soluble in water than other formates, 1 part dissolving in 63 parts of water at 16°, and is insoluble in alcohol; the solution forms a series of basic formates on being warmed with lead oxide, which have an alkaline reaction and crystallise in needles. *Copper formate* $(HCO_2)_2Cu,4H_2O$ crystallises in light blue monoclinic prisms: forms basic salts, $Cu(HCO_2)\ 2Cu(OH)_2$ and $Cu(HCO_2)_2,3Cu(OH)_2$ (Trans. Chem. Soc. 1915, 1281). Silver and mercurous formates decompose even in the dark, and the latter deflagrates when heated and decomposes on percussion. Chromous formate $Cr(HCO_3)_2{\cdot}2H_2O$, red cubes (Ber. 1916, 1679). *Methyl formate* boils at 30·4° (712 mm.), sp.gr. 0·9928; it is best made by acting on dry sodium formate with a mixture of methyl alcohol and aqueous hydrochloric acid, or by digesting methyl alcohol with concentrated formic acid. *Ethyl formate* boils at 50·4°, and has sp.gr. 0·9445 at 0°. It is made by heating a mixture of 6 parts of alcohol (90 p.c.), 7 parts of sodium formate, and 10 parts of concentrated sulphuric acid.

FORMICIN, FORMIDIN *v.* SYNTHETIC DRUGS.

FORMINS are esters produced by the condensation of glycerol or other polyhydric alcohol with formic acid.

Monoformin $HCO{\cdot}OC_3H_5(OH)_2$ is produced in the preparation of formic acid by heating glycerol with oxalic acid at 190° (Tollens and Henninger, Bull. Soc. chim. [ii.] 11, 395), and is extracted from the mixed product by means of ether. It is also prepared by the interaction of monochlorhydrin and sodium formate at 160° (van Romburgh, Rec. trav. chim. 1, 186). On distillation under atmospheric pressure it decomposes into carbon dioxide, water and allyl alcohol, but may be distilled unchanged *in vacuó.*

Dinitroformin is a yellow oil, sp.gr. 1·5 at 15°. It is formed together with nitroglycerin by heating anhydrous oxalic acid with glycerol at 150° and treating the product with nitrosulphuric acid (Vender, D. R. P. 209943; Chem. Soc. Abstr. 1909, i. 692).

Diformin $(HCO{\cdot}O)_2C_3H_5{\cdot}OH$ is the chief constituent of the residue obtained in the preparation of formic acid by heating anhydrous oxalic acid and glycerol at 140° (van Romburgh, J. 1881, 508). It is extracted with ether and purified by distillation under reduced pressure. B.p. 163°–166° under 20–30 mm.; sp.gr. 1·304 at 15°. Insoluble in carbon disulphide and decomposed by water with the formation of glycerol and formic acid. On heating under atmospheric pressure it is decomposed into carbon dioxide, water and allyl formate. With 5 parts of glycerol at 220°, carbon monoxide, carbon dioxide and allyl alcohol are the products, whilst with oxalic acid, carbon dioxide and formic acid are produced.

Triformin $(HCO{\cdot}O)_3C_3H_5$ is prepared by heating glycerol with excess of 100 p.c. formic acid. By cooling the viscous product by liquid ammonia, a crystalline mass is obtained. Pure triformin is colourless; has m.p. 18°; b.p. 266°/762 mm.; $n_D^{18°}=1{\cdot}4412$. It is saponified slowly by cold, readily by hot water (van Romburgh, Zeitsch. physikal. Chem. 1910, 70, 459).

By heating erythrol with formic acid and distilling off the acid at 200°, a mixture of formins is obtained, from which a tetraformin has been isolated. This forms silky needles, m.p. 150° (Henninger, Compt. rend. 98, 149).

FORMITROL (formolyptrol). Trade names for a preparation of formaldehyde.

FORMOL. Trade name for a preparation of formaldehyde.

FORMOLITES. A term applied to the various classes of phenol-formaldehyde, resins, *e.g.* lakelites, resinite, issolin, albertole, etc.

FORMOPYRINE. A compound of antipyrine and formaldehyde $C_{11}H_{13}ON_2{\cdot}CH_2O$; m.p. 142°; insoluble in cold water, soluble in chloroform and alcohol. Forms salts with acids (Marcourt, Bull. Soc. chim. 1896, 520). Stolz (Ber. 1896, 29, 1826) and Pellizzari (Gazz. chim. ital. 1896, 26, ii. 407) state that Marcourt's 'formopyrine' is identical with methylene diantipyrine $CH_2(C_{11}H_{12}ON_2)_2$, described by Pellizzari (Chem. Soc. Abstr. 1890, 645).

FORMOSE *v.* CARBOHYDRATES.

FORMURAL. Trade name for an addition product of hexamethylenetetramine and sodium citrate.

FORMUROL. An additive compound of hexamethylenetetramine and sodium citrate. Used as a urinary antiseptic.

FORNITRAL. Trade name for a compound of two mols. of formic acid with one mol. of endo-anilo diphenyldihydrotriazol $(HCOOH)_2(C_6H_8)_3(N_4C_2H)$. Used for the detection and estimation of nitric acid instead of nitron (Ann. Chim. Anal. 1921, 3, 207; Analyst, 1921, 385).

FORSTERITE *v.* OLIVINE.

FORTOIN. Methylene-dicotoïn

$CH_2(C_{14}H_{11}O_4)_2$

Formed by the action of formaldehyde on cotoïn. Used in the treatment of diarrhœa.

FOSSIL RESINS *v.* RESINS.

FOWLER'S SOLUTION. A solution of potassium arsenite.

FRACTIONAL DISTILLATION *v.* DISTILLATION.

FRAGARIANIN *v.* TANNINS.

FRANCKEITE. A complex sulphide ore of tin, $Pb_5FeSn_3Sb_2S_{14}$, containing, according to this formula, Sn 16·71 p.c. It consists of platy, tetragonal crystals, with a perfect cleavage parallel to the surface of the folia, which are often aggregated in more or less pronounced radiating groups, sometimes forming spherules and reniform masses. It is iron-black with a bright metallic lustre; marks paper and is malleable, like graphite. The mineral occurs in some quantity near Chocaya and in the Trinacria mine at Poopó in Bolivia, and is known locally as *llicteria*. The above formula written in the form $3PbSnS_2+Pb_2FeSb_2S_8$ brings out a relation between franckeite and the allied Bolivian minerals teallite ($PbSnS_2$) and cylindrite ($3PbSnS_2+SnFeSb_2S_8$). Analyses I and II by G. T. Prior, 1904 (II on less distinctly crystalline material with some massive), III by C. Winkler, 1893 (also germanium about 0·1 p.c., and gangue 0·71 p.c.) :—

	I.	II.	III.
Pb . .	46·23	48·02	50·57
Fe . .	2·69	2·74	2·48
Zn . .	0·57	—	1·22
Ag . .	0·97	0·99	n.d.
Sn . .	17·05	13·89	12·34
Sb . .	11·56	13·06	10·51
S . .	21·12	20·82	21·04
	100·19	99·52	98·87
Sp.gr. .	5·88	5·92	5·55

L. J. S.

FRANGULIN *v.* GLUCOSIDES ; also CASCARA SAGRADA.

FRANKINCENSE *v.* OLIBANUM ; art. GUM RESINS.

FRANKLINITE. A member of the spinel group of minerals with the general formula $R''O{\cdot}R_2''O_3$, where R''=Fe, Zn, Mn, and R'''=Fe, Mn. The actual composition is very variable; ferric oxide always predominates (56–67 p.c.), zinc oxide ranges from 6 to 23 p.c., and manganese oxides (MnO, Mn_3O_4) average 15–20 p.c. The mineral occurs as well-developed crystals of octahedral habit, as rounded grains, and as granular masses. It is black with a sub-metallic lustre, much resembling magnetite in appearance, but is readily distinguishable from this in being only slightly magnetic. Sp.gr. 5·0–5·2 ; hardness, 6.

Although known only from Franklin in New Jersey (hence the name), it is found there in considerable abundance in association with ores of zinc in crystalline limestone. After the extraction of the zinc, the residue is used in the manufacture of spiegeleisen. L. J. S.

FRAXETIN *v.* HORSE CHESTNUT.

FRAXIN *v.* GLUCOSIDES ; also HORSE CHESTNUT.

FRAXITANNIC ACID *v.* TANNINS.

FREDO. Trade name for calcium hydrosulphite.

FREESTONE. An indefinite term used by quarrymen for a rock which admits of being freely worked in any direction for use as a building stone. Such a rock shows a uniformity or evenness of grain and no distinct bedding. Many stratified rocks may be readily sawn when freshly quarried, and while holding the 'quarry-water,' but acquire considerable hardness on exposure to the atmosphere. Most freestones are either limestones or sandstones. In the Inferior Oolite there are certain beds known to geologists as the Lower and Upper Freestones, which are largely quarried as building stones, near Cheltenham. The Bath stone from the Great Oolite, and the Portland stone from the Upper Oolites, are also well-known Oolitic freestones. The term freestone is also applied to many of the red Permian and Triassic sandstones of the north-west of England, *e.g.* the St. Bees sandstone. Many of the Coal-measure sandstones admit of being readily cut and tooled, and, being without any marked tendency to split in definite directions, are valuable freestones : such, for instance, are the sandstones of Craigleith, near Edinburgh, and of Darley Dale in Derbyshire. L. J. S.

FREIBERGITE *v.* FAHLORE.

FRENCH CHALK. A variety of steatite, or soap-stone, used for marking cloth and for removing grease from silk. It is a hydrated magnesium silicate, with a smooth unctuous feel. In a powdered state it is sprinkled inside new gloves and in the heels of boots to produce a smooth surface and enable them to be readily slipped on (*v.* STEATITE).

FRENCH GREEN, EMERALD GREEN *v.* PIGMENTS.

FRENCH POLISH. A solution of shellac in alcohol ; occasionally containing gum elemi and copal.

FREUND'S ACID (1-Naphthylamine-3 : 6-disulphonic acid) *v.* NAPHTHALENE.

FRITTS and GLAZES. The 'glaze' of pottery is a vitreous coating, which serves to make the articles impervious to liquids, and may also be used for decorative purposes. According to the context, however, the word is also employed to denote (1) the mixed and powdered dry materials to be used for the coating, or (2) an emulsion of these materials suspended in water (' wet glaze ').

Usually the glaze is applied by dipping the dry or ' biscuit ' ware into this emulsion. The water soaks into the porous ' body,' leaving a deposit of the solid materials on the surface. When the ware is subsequently heated to a sufficiently high temperature, this layer melts, forming a glassy coating fused more or less completely with the underlying body of the article. Sometimes, however, the glaze is poured over the ware, or sprayed upon it, or dusted on as a dry powder, instead of being applied by ' dipping.' In the special case of salt glaze (used for stoneware), the salt is volatilised on to the ware in the kiln during firing.

The normal quantity of dry glaze on table and toilet ware ranges from about 4 to over 9 p.c. of the weight of the ware, the average being between 6 and 7 p.c.

A good glaze should be clear, bright, and uniform ; hard enough to resist wear ; and in the case of domestic and sanitary articles, should withstand the action of all the ordinary acids.

Defects.—Two principal defects to which the glaze on ware is prone are (1) ' crazing,' and (2) ' scaling ' or ' moulting.' In the first, a network of fine cracks spreads over the glaze ; in the second, the glaze chips off at the edges. They are usually accounted for as follows :—

Broadly speaking, the coefficient of expansion of a glaze should be that of the underlying ' body.' If, on cooling, the glaze contracts much more than the body, it is under tension, and either at once or during subsequent usage it yields to the stress, and cracks. The ' crazing ' may not develop for several months. In some ware—*e.g.* tiles—crazing is not of itself a serious fault ; in fact, makers hold that the refraction effects which result render the ware more artistic. The purchaser, however, may be prejudiced against it ; and in the case of table ware there is the additional objection that the cracks may harbour dirt and micro-organisms.

On the other hand, if the glaze contracts much less than the body, it is under pressure when cold, and portions chip off, even sometimes breaking the body itself. This ' scaling ' or 'moulting' is a less frequent evil than crazing. Moreover, it usually shows itself immediately after firing, and a remedy can thus be looked for before turning out further similar goods.

Other reasons for crazing are given in some cases. Thus 'short-fired' glaze, where fusion with the body is imperfect, is prone to craze.

Either the body or the glaze, or both, may be modified to remedy crazing. In the glaze, the proportion of alkalis is diminished, or that of the lime, silica, or boric oxide increased.

Composition.—Glazes after fusion are either alkali silicates (salt glaze), or silicates and borosilicates of aluminium, alkalis, and the alkaline earths, with or without lead. In coloured glazes, various colouring oxides, *e.g.* those of cobalt, copper, iron, manganese, are also present. Before fusion, the glaze may be merely common salt or felspar; but the usual materials of glazes are certain natural silicates, namely felspar, china clay or kaolin, and Cornish stone, mixed with flint or sand, chalk, borax or boric acid, soda, white lead, red lead, and litharge. Cullet (broken glass) is also sometimes an ingredient, and for course earthenware glaze, galena.

Fritting. Borax, boric acid, and soda, however, being soluble in water, would pass into the porous body of the biscuit ware during dipping if they were merely mixed with the other ingredients of the wet glaze. Hence they must be made insoluble in water. This is done by fusing them with a portion of the other ingredients containing lime, alumina, and silica, and the complex borosilicate thus obtained is a 'borax fritt.'

By 'fritt,' therefore, is to be understood certain ingredients of a glaze, which have been mixed and subjected to a preliminary fusion before being ground up with the remaining materials. Occasionally, the whole of the ingredients may thus be formed into a 'fritt.'

When lead is a constituent of the glaze, fritting is also advantageous, for two reasons: (1) it can thus, with due care, be rendered almost insoluble in dilute acids, and therefore much less dangerous to the health of the workers than when in the 'raw' form of oxide or carbonate; (2) the high density of 'raw' lead tends to make it settle down in the dipping tub more rapidly than the lighter ingredients do, thus making the glaze less uniform; this tendency is largely counteracted by having the lead in the form of a fritt. This, of course, also applies to other heavy materials, such as barium carbonate. Other cases where fritting is beneficial are when an ingredient is present in very small proportion, since it is then distributed more evenly; or when certain of the constituents are fusible with difficulty at the temperature employed for 'firing' the ware. A higher temperature may be used for the fritting, and much of the chemical work done which, with the 'raw' glaze on the ware, would have to be performed at a less effective temperature.

On the other hand, a certain proportion of material in the 'raw' state, especially clay, is advantageous for keeping the glaze suspended in water for dipping; hence it is not usual for all the ingredients of a glaze to be fritted.

Formulæ of glazes. In ceramic calculations it is customary to express the chemical formula of a glaze in terms of molecular 'equivalents' the sum of the RO constituents being made unity. Thus the glaze described on p. 248 will reduce to $1RO,0·27Al_2O_3,3·5(SiO_2,B_2O_3)$. Typical English glazes similarly work out as follows:—

	RO	Al_2O_3	SiO_2,B_2O_3
China . .	1	0·31	3·57
Earthenware .	1	0·26	2·80
Granite . .	1	0·32	3·43

The theoretical acids corresponding to the above four formulæ, expressed as ratios of $H_2O : SiO_2$, are respectively 1 : 2·1, 1 : 1·9, 2 : 3·1, and 4 : 7. That is, the four glazes lie between the bisilicate type ($H_2O,2SiO_2$) and the polysilicate ($2H_2O,3SiO_2$). Seger gives for white ware glazes the limits $1RO,0·1Al_2O_3,2·5SiO_2$ and $1RO,0·4Al_2O_3,4·5SiO_2$. The first is somewhat less acid than a bisilicate, the second rather more. A soft, heavily loaded English majolica glaze, however, $1RO,0·16Al_2O_3,1·68(SiO_2,B_2O_3)$, corresponds to $7H_2O,8SiO_2$, and is but slightly more acid than a monosilicate.

Lead glazes. The number of recipes for these is legion, but on calculating them out to the constituent oxides, they reduce to a few main types. They may be broadly classified as follows:—

(1) *China, earthenware, granite, ironstone,* and *semi-porcelain.* Contain 12–20 p.c. of PbO, occasionally more, usually about 17 p.c.

(2) *Rockingham, jet,* and *majolica.* 25–50 p.c. of PbO. Rockingham glazes contain Mn_3O_4, and jet CoO. Many majolica glazes have from 25 to 35 p.c. of PbO; the 'soft' varieties 40–50 p.c.

(3) *Tile glazes.* Usually 40–50 p.c. of PbO; the harder varieties less; in the softer kinds as much as 60 p.c.

(4) *General coloured glazes.* Described later; the proportion of PbO in these varies widely.

Examples showing the general percentage composition are:

	Granite	China	Rockingham	Jet	Soft majolica	Soft tile
SiO_2 .	54·8	50·8	35·6	34·8	32·3	32·6
PbO .	12·9	17·6	42·1	55·0	48·1	59·1
Al_2O_3	10·1	9·1	8·7	5·2	5·9	5·3
CaO .	4·8	5·4	2·9	1·2	3·8	0·8
Na_2O .	7·5	3·8	2·4	0·6	3·5	—
K_2O .	3·8	4·8			2·5	2·2
B_2O_3 .	6·1	8·5	0·7	—	3·9	—
Mn_3O_4	—	—	6·1	—	—	—
CoO .	—	—	—	2·1	—	—

Other things being equal, the larger the proportion of lead the 'softer' is the glaze, and the lower the temperature of firing. There is little doubt that for this reason more lead than is really necessary is often used.

Lead fritts. Lead oxides and carbonates are readily dissolved by the acid of the gastric juice, giving rise to plumbism. By suitable fritting, however, complex silicates containing lead, alkalis, alumina, and lime can be obtained of such character that, even when finely powdered, dilute acids attack them very slightly.

To be of this insoluble character, the complex silicate must not be more basic than would correspond to the metapolysilicic acid $H_4Si_3O_8$ (Chem. Soc. Trans. 79, 803-804). Preferably they should be less basic. Moreover, only a limited proportion of boric oxide appears to be admissible if the silicate contains a large percentage of lead, and the materials must, of course, be thoroughly fused. Previous fine grinding and good mixing are important in securing such fusion. Under these conditions, lead fritts may be made containing any proportion of lead up to 50 p.c. of PbO or over, but yielding only a very small quantity of lead to the action of dilute acids. The other bases may also vary considerably in their proportions, replacing one another and the lead oxide within wide limits, without notably affecting the amount of 'soluble' lead :

	PbO	Al_2O_3	CaO	$(Na,K)_2O$	PbO dissolved
1.	16·2	10·3	8·5	9·2	1·7 per cent
2.	44·1	5·5	0·9	3·4	2·1 ,,

Simple lead bisilicate $PbSi_2O_5$, containing theoretically 65 p.c. of PbO, and in practice about 60–63 p.c., is also used, but is somewhat more attackable by acids than the complex silicates. Nevertheless, there are some advantages attending the use of the simple bisilicate. The proportion of PbO in it being very high, less of the fritt is required to furnish a given amount of PbO in the glaze; this leaves so much the more room for clay and other materials to be used raw, if desired, to facilitate suspension of the materials in the water of the dipping tub. It implies, too, a minimum of alteration in changing from a raw lead glaze to one with fritted lead. For example, if the 17·6 p.c. of PbO in the china glaze, mentioned in the table above, were supplied by lead bisilicate, nothing but 9·5 p.c. of SiO_2 would have to be taken from all the rest of the materials. Without pressing this point unduly—for it should not be forgotten that the complex lead polysilicates may contain as much as 50 p.c. of PbO, and still be of 'insoluble' character—its importance will easily be recognised. The bisilicate is chiefly of value for the more heavily leaded glazes, Rockingham, jet, and majolica. The quantity of 'soluble lead' (*v. post*) extractible from commercial samples of the bisilicate is from 4 to 8 p.c.; hence majolica glazes containing 30–40 p.c. of total PbO would yield only 2–5 p.c. of 'soluble lead' if compounded by means of the bisilicate.

Simple lead polysilicate, $Pb_2Si_3O_8$, yields more soluble lead than the bisilicate; and from the monosilicate, $PbSiO_3$, the whole of the lead is easily dissolved. Even the complex silicates, if of the monosilicate type, H_2SiO_3, readily yield up a large proportion of their lead to the action of dilute hydrochloric acid. Lead fritts of this (monosilicate) character were almost the only form of 'fritted lead' used in the English potteries up to a few years ago, and it is not surprising that they gave rise to cases of lead poisoning.

Complex lead polysilicates and bisilicates containing alumina yield less soluble lead than the corresponding simple lead silicates. There is evidence to show that the alumina renders the silicate more stable—perhaps by acting as an acidic oxide (Chem. Soc. Trans. 97, 2286).

Where fritts contain only small quantities of 'soluble' lead—say up to 3 p.c. or so—one treatment of the ground fritt with dilute hydrochloric acid removes nearly all this soluble lead, which there is reason to believe is usually present as an admixture of silicate more basic than the bulk. On subsequently testing the residue, mere traces of lead are extracted.

The various forms of lead fritt are heavy glass-like substances of yellow colour. They should be of uniform texture, showing no fragments of unfused materials. They have no sharp melting-points; when heated they soften gradually until fused. Vitreous silicates, however, conduct electricity (Doelter), and the relative fusibilities of fritts may be compared by determining the temperatures at which the coarsely powdered fritts soften and blend into a continuous mass, such as will allow the passage of the electrical current. As thus determined, the 'softening-points' of some simple lead silicates are as follows: PbO,SiO_2, 480°, $PbO,2SiO_2$, 570°; $PbO,3SiO_2$, 620°. The inclusion of boric acid or borax in the silicate lowers these softening-points; lime or alumina raises them (Beck, Löwe, and Stegmüller; *v.* reference at end of article).

Effect of fine grinding upon solubility of the lead. For a full discussion of this, *see* Manchester Memoirs, vol. 45 (1901), No. 15, or Parliamentary Paper Cd. 679 on Lead Compounds in Pottery, 33. The conclusion is that fineness of subdivision is not absolutely without influence upon the quantity of lead dissolved: but that within the limits of fineness occurring in actual practice the effect is too small to be of serious moment.

Method of determining the 'soluble' lead. The British official method is as follows: 1 gram of the dried glaze or fritt, ground ready for use, is shaken continuously for an hour with 1000 times its weight of 0·25 p.c. solution of hydrochloric acid. After being allowed to settle for an hour, an aliquot part is filtered off, silica separated by evaporation in the usual way, the lead precipitated as sulphide, and finally weighed as sulphate.

In the United Kingdom potters who use no glaze yielding more than 5 p.c. of 'soluble lead' (PbO), as thus tested, are exempted from certain restrictions. Further exemptions are allowed where the glaze used gives not more than 2 p.c. of such soluble lead. If the total amount of lead is not more than 1 p.c. (calculated as PbO), the glaze is classed as 'leadless,' and this carries with it additional privileges.

Percentage composition of some complex lead silicates, with the amounts of PbO dissolved from them by 0·25 p.c. HCl :—

No. Type	PbO	CaO	$(Na,K)_2O$	Al_2O_3	B_2O_3	SiO_2	P.c. PbO dissolved
1. Bisilicate .	21·8	8·5	3·8	7·4	3·8	54·4	traces
2. ,, .	44·1	0·9	3·4	5·5	—	44·7	2·1
3. Polysilicate	16·2	8·5	9·2	10·3	5·8	49·7	1·7
4. ,, .	41·1	2·1	5·9	7·2	—	43·6	3·0
5. Monosilicate	37·9	10·8	3·7	8·2	—	37·6	28·0
6. ,, .	70·3	0·5	1·6	1·1	2·6	23·9	70·3

Fritts similar to Nos. 2 and 4 are the more generally useful for compounding glazes. Those like Nos. 1 and 3, containing less PbO and more SiO_2, have more restricted application; and Nos. 5 and 6, in so far as soluble lead is in question, are quite inadmissible.

The proportion of lead-oxide dissolved from a few fritts containing 57–63 p.c. of PbO, and approximating to lead bisilicate in composition, is appended:

PbO present, p.c.	57·3	58·5	59·3	63·4
PbO dissolved ,,	2·6	4·2	5·1	7·2

If these fritts are used to supply the lead in glaze containing 15 p.c. of lead oxide, the amount of soluble lead in such glaze will range from 0·7 to 1·7 p.c.

The German official method is to heat for half an hour with a 4 p.c. solution of acetic acid. Petrik has suggested a much more stringent method (Sprech Saal, 1914, 47, 1). It consists in digesting 5 grams of the finely-ground substance for an hour with 150–200 c.c. of 0·33 p.c. hydrochloric acid at 37°–40°. Sodium acetate is then added to promote settling and to dissolve lead chloride. The residue after filtration is also washed with sodium acetate solution. Lead is then estimated as sulphate. In a comparison of these methods, a glaze which had a solubility of 0·17 p.c. PbO by the English official method, yielded 0·25 by the German official method, and 0·56 by Petrik's method.

Lead dissolved from finished ware. Lead may be extracted by acids from the glaze on the fired article, as, for example, by vinegar or fruit acids from culinary vessels. There is evidence to show that, speaking broadly, the more 'soluble' lead there is in the glaze before firing, the more it is liable to be extracted from the glaze on the finished article. The actual quantity, however, is less from the fired glaze than from the original, on account both of the smaller surface presented and of the chemical changes resulting from the fusion.

Compounding of glazes. In compounding glazes from the raw materials regard must be had to several considerations besides the formula and the analytical composition. The proportion of clay, for instance, influences the shrinking of the glaze before firing; too much causes a tendency to flake off. Again, it may be that sufficient alkali cannot be introduced as felspar or stone without adding too much alumina; some alkali must then be included as a fritt, which may also contain the borax and the lead, if these are constituents of the glaze. An example from actual practice will illustrate the compounding of a glaze by the use of fritts.

The proximate composition of a certain glaze used for earthenware and china is given[1] as: SiO_2 50·9, PbO 17·0, Al_2O_3 7·7, CaO 7·6, $(Na,K)_2O$ 6·0, and B_2O_3 10·8 p.c. To obtain all the advantages of fritting, two fritts must be made, one to contain the lead, and the other the boric oxide; for if a single fritt contained both, the high proportion of boric oxide would render the lead too easily soluble in acids, and thus one important advantage of fritting would be lost. A lead fritt is therefore made by fusing: litharge 39, flint 21, orthoclase and oligoclase felspars, each 10 parts: and a borax fritt by fusing: borax 150, flint 75, china clay 50, and whiting 50 parts. The calculated composition of these two fritts, allowing for the CO_2 and H_2O expelled on heating, is as follows:—

	SiO_2	PbO	Al_2O_3	CaO	Na_2O	K_2O	B_2O_3
Lead fritt	42·3	48·8	5·1	0·6	1·1	2·1	—
Borax fritt	43·1	—	8·5	13·1	11·1		24·2

(In practice, however, a little lead is lost by volatilisation and by fusion with the walls of the 'sagger' during fritting. Actual analysis of the lead fritt showed 44·1 p.c. of PbO, the proportions of the other constituents being correspondingly increased.)

To form the glaze, these two fritts are then combined with raw materials, flint, china clay, and whiting, in the proportions: lead fritt 205, borax fritt 260, flint 81, china clay 34, and whiting 20 parts. The lead fritt, it may be noted, would have the same composition if it were made from the following ingredients: Cornish stone 25, litharge 48½, flint 25½, soda, calcined, 2 parts. This dispenses with the felspars.

Coloured glazes. So far as the glaze is concerned, coloured ware is obtained (1) by applying the colouring materials to the raw or biscuit body, which is afterwards glazed with a transparent glaze ('*under-glaze*' process); (2) by placing the colouring materials on the already glazed article, and refiring it ('*on-glaze*' process); or (3) by embodying the colour in the glaze itself ('*coloured-glaze*' method).

For the last-named process, a fritt may be made to contain the colouring oxide in chemical combination, and ground up with the other materials to form the glaze. Alternatively, a lead fritt or glaze may be taken as colourless fusible basis, and colouring oxides ground up or fritted with it.

The first of these two methods, for example, is that adopted by Messrs. Villeroy and Boch, Dresden. Their colourless[2] glaze for earthenware has the chemical formula:

$$1RO,0{\cdot}33Al_2O_3,3(SiO_2,B_2O_3)[8SiO_2 : 1B_2O_3].$$

Its molecular and percentage composition are:

	K_2O	Na_2O	CaO	PbO	Al_2O_3	B_2O_3	SiO_2
Mols.	0·25	0·75	1·50	2·00	1·50	1·50	12·00
P.c.	1·49	2·94	5·31	28·17	9·68	6·63	45·78

For convenience of dipping, 15 p.c. of the materials are left unfritted, the remainder being made into a fritt, as follows:—

	Felspar	Chalk	Litharge	Sand	Borax	Potsherds	Kaolin
Fritted	3·5	5·4	24·7	18·5	15·4	17·5	—
Raw	3·0	2·9	—	—	0·5	—	8·6

For coloured glazes, the CaO in the fritt is replaced by CoO, CuO, NiO, &c., or the Al_2O_3 by Fe_2O_3, Mn_2O_3, Cr_2O_3, U_2O_3, &c. These coloured fritts are then diluted with the colourless glaze to the desired tints.

The second method is exemplified as follows (Salvetat): The materials of a colourless flux, namely, calcium borate, flint, and red lead, are mixed in the proportions of 1 : 2 : 4; this mixture with 1–4 p.c. of CoO gives blues; with 3–14 p.c. CuO, greens; with 2–6 p.c. Fe_2O_3, yellows: and so on. All the ingredients are fritted to facilitate perfect mixture. An English colourless fritt for similar purposes is made by fritting: flint 10, china stone 9, red lead 30, and borax 4 parts: this is ground and mixed with various colouring oxides.

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[1] Almstrom, Lead Compounds in Pottery (Parliamentary Paper, C9207, p. 24).

[2] Lead Compounds in Pottery, Cd. 679, p. 21.

Enamels are opaque glazes, the opacity being due to tin oxide in suspension. In this country, however, the term 'enamels' (enamel colours) is also applied to the colours used for 'on-glaze' decoration.

White enamel may be obtained (Brongniart) by fritting calcine (= mixed oxides of lead and tin), sand, soda, and salt. Various proportions are used, a general formula being SiO_2 45, PbO 36, SnO_2 10, and NaCl 9 p.c. Coloured enamels result from the addition to this of 3-10 p.c. of colouring oxides. Thus 9 p.c. of lead antimonate, 5 of CoO, 5 of CuO, and 4 of MnO_2, give yellow, blue, green, and violet respectively.

Colours. *Under-glaze* colours are generally oxides or chromates, with flint, whiting, Cornish stone, or fluxes containing borax or lead. *On-glaze* colours are fusible glasses, composed usually of a lead borosilicate flux with colouring oxides. A common flux ('No. 8') used in this country consists of flint, borax, and red lead in the proportion of 1 : 2 : 3, but various proportions are employed.

Leadless glazes. The salt glaze used for *stoneware* has already been mentioned. For *hard porcelain*, the glazes employed are (1) 'alkaline' or felspathic glazes, consisting of silicates of alumina, alkalis, and alkaline earths, in which the alkalis preponderate over the lime and magnesia; and (2) 'calcareous' glazes, similar to (1), but in which the lime exceeds the alkalis. The materials used are pegmatite, with an addition of silica to modify the fusibility, or a mixture of felspar, quartz, and kaolin, with or without chalk.

For *soft porcelain*, *china*, and *earthenware*, glazes containing boric oxide are usually employed. One recipe for such glaze is: felspar 48·7, borax 27·0, whiting 13·5, and flint 10·8 p.c. This is fritted, and mixed with one-third of its weight of china clay to form the glaze.

Analytical Composition of various Leadless Glazes.

	Pegmatite[1] (Sèvres)	Calcareous[1]	English[2]	
			Minton's	Owen's
SiO_2 . .	70·6	64·8	57·5	50·4
Al_2O_3 & Fe_2O_3	17·6	15·7	14·7	12·2
CaO . .	1·3	10·1	8·5	12·1
MgO . .	0·2	1·5	0·2	0·5
Na_2O . .	5·0	0·8	3·8	8·3
K_2O . .	4·2	5·6	4·1	2·5
B_2O_3 . .	—	—	10·7	10·7
CO_2 . .	—	—	—	2·5

'Leadless' glazes not infrequently contain traces of lead, arising probably from their having been ground in mills previously used for lead glaze. Occasionally larger quantities are found, due to the use of flint glass as an ingredient.

Ware coated with leadless glaze may, on analysis, show traces of lead in the glaze, not only from the foregoing causes, but also from having been fired in a lead-washed sagger, or in proximity to lead-glazed goods. Lead in one form or another may be volatilised from the latter, and some of the lead vapours are absorbed by the leadless glaze. It is not difficult, however, to distinguish between such ware and that glazed with ordinary lead glaze. In the glaze removed from a definite area of the ware by means of hydrofluoric acid, the lead is determined; the proportion on leadless-glazed ware is usually less, and often much less, than 0·1 gram PbO per square decimetre; whereas that on lead-glazed table ware ranges from about 3 times to 8 times this quantity, and on heavily-leaded ware, such as tiles, it may be upwards of 40 times as much.

As regards the suitability of leadless glazes for pottery, it may be said that in all classes of ware a great many articles can be manufactured with leadless glaze, in a very high state of perfection. The cost of production in the commonest qualities is less than with lead glaze, and in some others is not appreciably greater. But in certain of the best and medium classes there is an undue proportion of 'seconds,' that is, ware not of the highest finish, and this raises the cost or lowers the quality. It is not clear, however, that this is due to anything inherent in the use of leadless glaze. For certain colours and methods of decoration leadless glazes at present cannot replace those made with lead. On the other hand, there is no doubt that a great deal of white and cream-coloured ware for domestic, sanitary, and electrical purposes, now coated with lead glaze, could be glazed without the use of lead.

For a summary of present knowledge and experiments respecting soluble lead in fritts and glazes, *see* Beck, Löwe, and Stegmüller, Zür Kenntniss der Bleihaltigen Glasuren und deren Bleiabgabe an saure Flüssigkeiten (Arbeiten aus dem Kaiserlichen Gesundheitsamte, Band 33, Heft 2, 1910). C. S.

FRUCTOSE *v.* Carbohydrates.

FUCHSIA. The chlorides of α- and β-dialkylsafranines are met with in commerce under this name (*v.* Azines).

FUCHSIN, RUBIN, ROSEIN, MAGENTA (*v.* Triphenyl methane colouring matters).

FUCOSE. Carbohydrates.

FUCITOL. An alcohol, $C_6H_{14}O_5$, m.p. 153°–154°, obtained by reducing fucose (*q.v.*) by sodium amalgam. Is the optical antipode of rhodeitol. In presence of borax in aqueous solution its rotatory power was $[\alpha]_D^{20}=+4·7$, and when mixed with an equivalent quantity of rhodeitol in hot alcoholic solution, it yields racemic fucitol (*d*-, *l*-rhodeitol), m.p. 168°–170° (Votocek and Potmesil, Ber. 1913, 46, 3653).

FUCOSOL. This product which Stenhouse obtained by the distillation of certain *algæ* with dilute sulphuric acid (Proc. Roy. Soc. 20, 80), and which he considered as isomeric with furfurol, has been shown by Bieler and Tollens (Ber. 1889, 3062) and by Maquenne (Compt. rend. 109, 571) to be a mixture of furfurol and methyl-furfurol derived from pentaglycoses contained in the *algæ* (*v.* also Muther and Tollens, Ber. 1904, 298).

FUEL. This term includes all combustible substances obtainable in bulk which may be burned by means of atmospheric air in such a manner as to render the heat evolved capable of being economically applied to domestic or industrial purposes. Fuels may be divided into (a) *solid fuels*, including (i.) natural fuels, consisting of woody tissues in an unaltered (wood) or an altered form (peat, lignite, coal); (ii.) carbonised fuels (charcoal, coke); (iii.) compressed fuels (briquettes); (b) *liquid fuels* (petroleum, benzenes, alcohol); (c) *gaseous fuels* including (i.) natural gas; (ii.) gases produced by the carbonising of solid fuels (coal gas, &c.); (iii.) gases produced by the partial combustion of solid fuels (blast furnace gas, producer gas, water gas). All fuels, having been originally derived from some form of living matter, or the products of its alteration, are composed of the elements C, H, O, N, and S, together with (in the case of solid fuel) a variable amount of mineral matter, which constitutes the incombustible ash.

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[1] Bourry, Treatise on Ceramic Industries.

[2] Analysed in the Government Laboratory, London.

The economic importance of a fuel depends upon (1) its distribution; (2) its cost of production, transport, and storage in bulk; (3) the total amount of heat obtainable on burning unit weight of it; and (4) the rapidity, efficiency, and smokelessness of its combustion with atmospheric air. Of all natural fuels coal is by far the most important, for despite the probability that there is more combustible matter in the peat deposits than in all the known coalfields of the world, and the marked inferiority of coal to petroleum in respect of calorific value, no other fuel combines so many economic advantages as coal.

The calorific value, or the total amount of heat obtainable by the combustion of a given fuel, is expressed by the number of parts by weight of water which may be heated through 1° on the thermometric scale by the combustion of one part by weight (or, in the case of gaseous fuels, by volume at N.T.P.) of the fuel under conditions such that the whole of the heat of combustion is transferred without loss to the water, and that the products leave the system at atmospheric temperature and pressure. The metric unit of heat adopted for technical purposes (the K.C.U.) is the quantity of heat required to raise 1 kilog. of water through 1°C. in the neighbourhood of 15°C., whilst the British unit (the B.Th.U.) is the amount of heat required to raise 1 lb. of water through 1°F. in the neighbourhood of 60°F. Thus, 1 K.C.U. =3·9683 B.Th.Us., and 1 B.Th.U. =0·252 K.C.U.; moreover, in the case of solid or liquid fuels, a calorific value of xK.C.Us. per kilog, is equivalent to 1·8xB.Th.Us. per lb. (or, conversely, xB.Th.Us. per lb.=0·5555 xK.C.Us. per kilog.), whilst, in the case of a gas, xK.C.Us. per cubic metre is equivalent to 0·11236 xB.Th.Us. per cubic foot (or, conversely, xB.Th.Us. per cubic foot =8·90 xK.C.Us. per cubic metre). For purposes of calculation, the calorific value of a gas may often be expressed more conveniently in K.C.Us. per gram-molecule (*i.e.* 22·38 litres at 0°C. and 760 mm.) than in any other form; in such a case, xK.C.Us. per gram-molecule=44·68 xK.C.Us. per cubic metre at 0° and 760 mm., or 5·02 xB.Th.Us. per cubic foot at 0° and 760 mm.

In cases where hydrogen enters into the composition of a fuel, it is usual to differentiate between its *gross* and *net* calorific values, the former implying that the products of combustion have all been cooled down to atmospheric temperature (15°C.), the latter, that the heat liberated by the condensation of the steam produced on combustion and by the subsequent cooling of the water to 15° has not been included. The difference between *gross* and *net* values will always be 11·196 K.C.Us. per gram-molecule of steam produced on combustion (=622 K.C.Us. per kilog., or 1119·6 B.Th.Us. per lb.).

The determination of the calorific value of a solid or liquid fuel may be best carried out by burning a known weight of it in compressed oxygen in some form of bomb calorimeter, that known as the Berthelot-Mahler apparatus being well adapted for this purpose. In the hands of an experienced worker, the method is a very accurate one, provided that all the proper 'corrections' (*e.g.* for 'cooling' and for the formation of nitric acid) are determined and applied; it must be remembered, however, that the method gives the heat of combustion under '*constant volume*' and not under '*constant pressure*' conditions, and in the calculation of the latter from the experimental results a proper 'correction' must be applied. In the case of coals, the combustion of which is attended by very little change in chemical volume (*e.g.* 1 lb. of a coal containing C=80·0, H=5·5, S=1·0, N=1·5, O=5·0, and ash =7·0 p.c. requires 135·2 cubic feet of air, and yields 130·8 cubic feet of gaseous product at 0° and 760 mm.), the difference between the heats of combustion under 'constant volume' and 'constant pressure' is negligible in practice, but not so in the case of a hydrocarbon such as heptane

$$C_7H_{16}+11O_2=7CO_2+8H_2O.$$

The calorific value of a gas is usually determined by burning a measured volume of it at atmospheric pressure in a chamber surrounded by a system of coils or the like, through which a flow of water at a constant 'head' is maintained. By suitable regulation of the pressure and flow of the gas and water supplies respectively, the gas may be completely burnt and the heat developed transferred substantially without loss to the water, the products leaving the apparatus at a temperature only slightly above that of the atmosphere. Several forms of this apparatus are in use, the most satisfactory being those designed by Junkers and C. V. Boys respectively. With suitable modification (*e.g.* the provision of a differential thermojunction arrangement for registering the rise in temperature of the water on a moving chart), the method can be made a 'recording' one.

The heat of combustion of amorphous carbon is 8080 K.C.Us. per kilog. when completely burnt to the dioxide, and 2417 when burnt to the monoxide; the values for the principal single gases (taken from Julius Thomsen's researches) are as follows:—

	K.C.Us. per gram molecule		B.Th.Us. per cub. ft. at 0° and 760 mm.	
	Gross	Net	Gross	Net
Hydrogen	68·4	57·2	343·3	287·2
Methane	212·0	189·5	1064·0	951·3
Ethane	370·5	336·9	1860·0	1691·0
Ethylene	333·3	310·9	1673·0	1561·0
Propylene	492·7	459·1	2474·0	2305·0
Acetylene	310·0	298·8	1556·0	1500·0
Carbon monoxide	68·0		341·4	
Cyanogen	259·6		1303	

The *gross* values for single liquid fuels, in K.C.Us. per kilog. are *n*-hexane=11,620, benzene =10,250, toluene=10,390, methyl alcohol=5694, ethyl alcohol=7400. According to Julius Thomson, an increase of $>CH_2$ in ascending an homologous series of hydrocarbons or alcohols corresponds to a constant increase of 158·5 K.C.Us. in the gross value of the molecular heat of combustion.

It is not possible to calculate the calorific values of compound fuels such as coal or petroleum from their elementary analyses, since the heat of combustion of a compound is never equal to the sum of those of its elements taken *proportionately*. In the case of bituminous coals empirical formulæ, such as:

$$Q = \frac{1}{100}[8080C + 34{,}460(H - \tfrac{1}{8}O) + 2250S]$$

K.C.Us. per kilog., where C, H, O, and S=percentage of carbon, hydrogen, oxygen, and sulphur, have been proposed for this purpose; but they cannot be considered as more than approximately correct. There is often a fairly close agreement between the results calculated by means of this formula and those actually found by the bomb calorimeter in cases where the oxygen content of the coal does not exceed about 7·5 p.c. In coals with a high oxygen content, however, there is usually a marked disagreement. On the other hand, since the properties of a gaseous mixture are additive in respect of its constituents, the heats of combustion of gaseous fuels of which the composition has been accurately determined by analysis (and this applies more particularly to such cases as water gas or producer gas, the combustible constituents of which are hydrogen, carbon monoxide, and methane only) may be calculated from those of their constituents. In the case of coal gas, where the composition of the heavy hydrocarbons absorbable by bromine is always uncertain, this rule is not strictly applicable, although numbers calculated on the assumption that the heavy hydrocarbons have an average calorific value equal to that of propylene C_3H_6, are generally not widely different from those determined by the calorimeter.

The so-called 'calorific intensity' of a fuel is an unscientific term, inasmuch as the highest temperature which a particular fuel is capable of producing depends entirely upon circumstances which are, to some extent, indefinable, and difficult of control. The notion that the calorific intensity of a fuel may be deduced by dividing its calorific power by the mean specific heat of its products, is misleading, inasmuch as (1) the specific heats of gases, and especially of steam and carbon dioxide, increase with temperature, and at high temperatures are as yet not accurately known; (2) part of the potential energy of a fuel is directly radiated away during combustion, and does not appear as sensible heat in the products; and (3) combustion is ordinarily not sufficiently instantaneous to warrant the assumption above referred to. The measurement of furnace temperatures and the like is, however, of great practical importance, and many instruments have been designed for this purpose (*see* PYROMETRY). These depend upon (1) the variations with temperature in the pressure (at constant volume) or volume (at constant pressure) of a gas which does not appreciably deviate from Boyle's law (air thermometer); (2) the production of thermo-electric currents (thermojunction methods); (3) the increase in the electrical resistance of a platinum wire with temperature (resistance methods); and (4) the variation with temperature of the radiation emitted by an incandescent solid as defined by Stefan's law (*radiation pyrometry*). Methods (1) to (3) inclusive, whilst capable of great accuracy, are practically useful up to temperatures of 1000°–1200° only; they can be made 'recording,' however, and are invaluable for recording the temperatures of hot gases passing into furnaces from 'regenerative' systems (hot-blast stoves, melting-furnace regenerators) or of hot products passing into chimneys. Method (4), whilst of relative significance only, is invaluable for temperatures higher than 1000°; as a modification of method (4) may be mentioned various forms of *optical pyrometers*, in which the light emitted by an incandescent surface is compared with that from a standard source (*e.g.* an amyl acetate flame).

A. SOLID FUELS.

1. *Natural Fuels.*

All natural fuels of this class have originated in cellulose $n(C_6H_{10}O_5)$, which, in fact, constitutes about 95 p.c. of dry woody tissue. The gradual transformation of vegetable *débris* into coal has proceeded during nearly all geological epochs. All the important coal-fields adjacent to the N. Atlantic and Arctic areas (which include nearly all those of N.-W. Europe and the E. part of N. America) originated in the Carboniferous Period of the Primary Era. The 'Indian Ocean' group of coal-fields (which include those of China, India, Australia, and S. Africa) originated in the somewhat later Permo-Carboniferous Period. Mesozoic coals are found in the interiors of N. America and Asia (intra-continental group); whilst Tertiary coals are chiefly found in the Pacific borderland (W. of N. America, Japan, and New Zealand), as well as in regions bordering on the Gulf of Mexico and the Mediterranean. The vegetable forms which flourished in the Carboniferous Period were of simpler structure, but of much greater size, than those which are predominant to-day (gigantic ferns, club mosses, horsetails, and forms intermediate between ferns and cycads), and it is demonstrable that in certain cases (*e.g.* the Moira seam near Loughborough in Leicestershire) entire beds of coal have been formed from the spores of such plants.

At one time it was generally believed that coal formation had taken place upon the actual site of growth, the requisite conditions being dense forests in swampy areas, together with oscillations of level, the coal-measures produced during a period of subsidence being overlaid by beds of water-deposited clay or sandstone, which, on re-elevation, formed the soil for renewed forest growth. Hence coal is found in strata of undoubted estuarine or lacustrine origin (Carboniferous, Jurassic, Cretaceous); the common occurrence of 'under-clays' in the coal-measures is cited in support of this hypothesis, which probably is true for some British coal-fields. It has been contended by some geologists that in many cases the transformation of vegetable *débris* into coal has taken place not upon the site of growth, but after transportation by river currents and deposition in deltas; it has also been suggested that certain coal-seams are of marine origin.

There has also been much speculation and diversity of opinion as to the nature of the transformation process, and the factors operative therein; it is usually supposed that its earlier stages were characterised by slow oxidation under water or other covering sufficient to protect the decayed wood from direct atmospheric action, and that supervening upon this were changes gradually brought about by increasing pressure and temperature as the deposits were overlaid and 'blanketed' by accumulating newer *strata*. The final transition from a bituminous coal to anthracite—if such, indeed, has taken place—may be attributed (i.) to intense earth pressure accompanied by seismic disturbance; or (ii.) to the later intrusion of igneous matter from below. It should, however, be stated that in some instances at least there are grounds for believing that anthracite has been formed from vegetable matter of a kind distinct from that concerned in the formation of bituminous coal, without necessarily passing through the intermediate 'bituminous' stage (*vide* section of this article on British Coal Fields (1) *South Wales*, p. 262). M. Renault, from an extensive study of peat formation, has advanced the hypothesis that the chief agents in the early stages of the transformation process have been certain aërobic fungi, and anaerobic bacterial ferments, the relative activities of which would depend upon the varying water-level in the bog and the formation of ulmic acid. He represents the transition from cellulose into bituminous coal by the equation:

$$4C_6H_{10}O_5 = C_9H_6O + 7CH_4 + 8CO_2 + 3H_2O.$$

(C_9H_6O would contain C=83·1, H=4·6, O=12·3 p.c., which approximates to the composition of many bituminous coals.) But whatever may have been the nature of the process, it is generally agreed that the existing coal-measures represent some 20–25 p.c. only of the weight of the original cellulose, and less than half of its heating value; in a few cases, where the original vegetable *débris* has undergone local 'petrifaction,' it has been established that the shrinkage in bulk during transformation into coal has been of the order 9 : 1 approximately. The composition and calorific values of the dry ashless cellulose and intermediate products up to coal itself is shown in the following table:—

	C	H	O and N	K.C.Us. per kilog.
Cellulose .	44·5	6·2	49·3	4107
Wood .	50·0	6·0	44·0	4000–4300
Peat .	50–64	4·5–6·8	28·6–44·0	5000–6000
Lignites .	60–75	5·0	20·0–35·0	6000–7000
Bituminous coals .	75–90	4·5–5·5	5·5–15·0	8000–9600
Anthracite	90–95	2·4	3·0	9200–9800

Wood when dry consists of about 95 p.c. of cellulose and 4 p.c. sap, associated with a small amount of mineral ash (chiefly $CaCO_3$ and K_2CO_3). Recently felled timber contains a large proportion of water which 'air-drying' reduces to about 20 p.c. An 'air-dried' wood is classed as 'hard' or 'soft' according as its sp.gr. exceeds or falls below 0·55; 'hard' woods are less inflammable than 'soft' varieties. As a fuel wood is very combustible, and burns with a great amount of flame; it is well adapted for domestic fires and the firing of tubular boilers, its low content of infusible ash making it a clean fuel without a vestige of 'clinkering' properties. Owing to its large content of hygroscopic water, it is quite unsuitable for the attainment of high temperatures, unless it first be carbonised (charcoal), or be gasified in a producer. On distillation in closed retorts or chambers it yields, under favourable conditions, 20–25 p.c. of charcoal, 9–13 p.c. of tar, 40–45 p.c. of crude 'pyroligneous acid' (corresponding to 2–4 p.c. anhyd. acetic acid), and 22–32 p.c. of inflammable gases. The chief timber-producing countries are those which before the war comprised the Russian Empire with 920 million acres of forests (575 in Europe and 350 in Asia), Canada with 800 million acres (of which probably less than half represents timber of commercial value), the United States, Norway, and Sweden with 70 million acres, and Germany with 35 million acres. Russia was, however, the only European country which before the war produced more timber than it required. It is as yet too soon to estimate the effects of the war upon timber supplies. The rapid demolition of the world's reserves is becoming a serious economic problem, and it is improbable that wood will ever again take important rank as a fuel.

In countries where wood, peat, or coal is scarce, vegetable refuse (cotton stalks, brushwood, straw, &c.) is used as fuel for tubular boilers; as a rule it has between 70 and 80 p.c. of the heating value of dry wood.

Peat is a widely distributed and abundant fuel of great future potentiality, it being estimated that the amount of combustible matter in the world's peat deposits exceeds that in all the known coal-fields. It is principally found in high latitudes; one-seventh of the area of Ireland is covered with peat, whilst in Great Britain there are about 6 million acres covered to an average depth of about 12 feet. Extensive deposits occur in Russia, where peat is an important metallurgical fuel, in Scandinavia, N. Germany, Bavaria, Austria, Italy, and N. France, to mention European countries only. Also considerable attention has recently been paid to peat deposits in Canada (*vide* Reports by A. v. Anrep and B. F. Haanel of the Canadian Department of Mines, 1912–1914). Peat deposits vary considerably in age, the oldest having a dark-brown or black colour, with but merest traces of its original organic structure, whilst the recent varieties are light-brown in colour, of spongy texture, with distinct vegetable structure; unlike wood, it contains a fairly large and variable proportion of mineral ash (5–15 p.c. as a rule) of (usually) infusible character. The composition of the ash varies considerably; sulphate and carbonates of lime and magnesia, ferric oxide, and silica being usually the most prominent constituents. The difficulty in the way of utilising the potential energy of peat for economic ends lies in the fact that even a well-drained peat-bog contains 80–90 p.c. of water, for the evaporation of which more energy would be required than is represented by the whole fuel-value of the bog.

Consequently, 'air-drying' has hitherto been universally resorted to, but as this can only be carried out during the summer months, and must obviously depend upon climatic conditions, it cannot be considered seriously as a means of preparing large quantities of peat for the market. Moreover, 'air-dried' peat still contains from 15 to 25 p.c. of water, its calorific value (which varies between 2235 and 4307, with an average of about 3000 K.C.Us. per kilog.) is usually considerably less than half that of a bituminous coal, whilst bulk for bulk its heating power probably does not exceed one-eighth that of coal. Dry 'ashless' peat contains C=50–64, H=4·7–6·8, O=28–44, and N=0·5–2·5 p.c., its cal. value=5200 K.C.Us. per kilog., and its sulphur content is low.

As recently as 1905 the Royal Commission on Coal Supplies reported that '*in order to make the manufacture of peat fuel a success in this country, it is necessary that some process should be discovered by which the moisture can be got rid of without "air-drying," and at a cost which would not be prohibitive; at present there is no such process.*' In 1909, however, the late Dr. M. Ekenberg prepared a process of '*wet carbonisation*' as a practical solution of the problem (Jour. Iron and Steel Institute, 1909, i. 313). This process was based upon the supposition that 'peat substance' consists of vegetable *débris*, the cells of which contain and are surrounded by a slimy '*hydrocellulose*,' formed by prolonged contact of the original cellulose with water. It was further supposed that although this constituent is present to the extent of 0·2–1·2 p.c. only, it is in the form of an enormously swollen jelly of the consistency of soft-soap, containing as much as 25 times its own weight of water, which latter cannot be expelled by mechanical pressure unless the supposed 'hydrocellulose' has been previously hydrolysed. It is claimed that this can, however, be rapidly accomplished by water at 150°–200°, forming the soluble dextrose, and peat pulp so hydrolysed readily parts with its water under hydraulic pressure. The Ekenberg process (as originally proposed) consists in forcing a peat pulp containing 12½ p.c. of peat substance and 87½ p.c. of water at 220–300 lbs. per sq. in. pressure through a series of tubes heated externally to about 200°, the operation being combined with a system of heat recuperation, whereby the outgoing hot 'carbonised' peat imparts heat to the incoming cold pulp. The 'carbonised' pulp is dehydrated by mechanical pressure, and the dehydrated fuel is subsequently briquetted. The process has not, however, advanced beyond an experimental stage, whilst doubts have been expressed as to the validity of the 'hydrocellulose' supposition on which it is based. Meanwhile, attempts have been made, with some measure of success, to expel the greater part of the water contained in raw peat by a process of mechanical pressure combined with a degree of heat materially below that proposed by Ekenberg. It seems possible that a pressed cake containing only 50 p.c. of water can be so produced, corresponding to the expulsion of nearly 90 p.c. of the water originally present in the raw peat, and that a solution of the peat fuel problem may ultimately be found in this direction.

The Fuel Research Board issued, in 1920, a report upon the "Peat Resources of Ireland" (Special Reports No. 2), and more recently a further report on "The Carbonisation of Peat in Vertical Gas Retorts" (Technical Paper No. 4), to which the reader is referred.

Peat containing as much as up to 60 p.c. moisture has been successfully gasified on a large scale in gas producers under ammonia recovery conditions (*vide* PRODUCER GAS); the following results have been obtained on Mond plants:—

Origin of peat	German	Italian	English
Per cent. moisture .	40–60	45	57·5
„ nitrogen .	1·0	1·58	2·3
Yield of gas in cub. ft. at 0° and 760 mm. per ton dry peat .	85,000	60,000	90,000
Gross cal. value of gas B.Th.Us. per cub. ft. at 0° and 760 mm. .	150	166	134

The richness of the gas depends upon the moisture in the peat; where the moisture is not excessive, the gas may contain as much as 35–40 p.c. of combustible constituents, *e.g.* $9·8CO$, $23·2H_2$, $4·8CH_4$, with $20·3CO_2$. It seems probable that a ton of dry peat is capable of yielding up to 90,000 cub. ft. of gas of an average gross calorific value of 140 B.Th.Us. per cub. ft. Part of this would be required to fire the boilers and to work the ammonia recovery plant, the remainder being available for heating or power purposes outside the plant. In addition to ammonium sulphate, it should be possible to recover other by-products (tar, acetate of soda or lime, acetone, wood spirit).

With regard to power production from peat (*via* gas producers and internal combustion engines) tests made at the Fuel Testing Station at Ottawa by the Canadian Department of Mines in 1910–1911 showed that the consumption of fuel per horse-power hour (including stand-by losses) is for fuel load, 1·7 lb., and for three-quarter load, 2·1 lbs. of *dry* peat.

Lignite and Brown Coals. Under this general term are included coals (intermediate between peat and bituminous coal) of Cretaceous or Tertiary age. They are widely distributed, (1) in what may be termed the 'Pacific Borderlands' (N.W. America, Japan, Australia, New Zealand, and the E. Indies); (2) in regions adjacent to, or in continuation with, the Gulf of Mexico; and (3) in regions north of the Mediterranean, including the Central European Plain. Cretaceous coals of the lignite class occur over a large area between lats. 49° and 43° N. and long. 100°–107° W. (the states of N. Dakota, Montana, and Wyoming) in N. America. Lignites occur also in Canada (Manitoba, Alberta, and Saskatchewan); whilst there are enormous deposits of brown coal in Australia (Victoria) of great potential value. Indeed the total thickness of the Gippsland deposits at Morwell (Victoria) amounts to about 780 ft. of coal within 1000 ft. of the surface; and it is anticipated that before long not only will the City of Melbourne derive the whole of its electric power from them, but also that the Victorian State Railways will be worked electrically from them. Classified according to external characters and geological age, lignites are usually divided into (1) woody or fibrous brown coal, with a distinct ligneous structure; (2) earthy lignite devoid of organic structure and easily powdered; (3) common brown coal, with a slatey cleavage and dark-brown colour, *e.g.* Bovey coal; and (4) bituminous lignite, pitch black in colour, and having a conchoidal fracture. Up to the outbreak of the war lignites were, relatively speaking, of little economic importance except in Germany and Austria-Hungary, where (in 1913) 87·1 and 27·4 million tons respectively were raised for home consumption. The war has, however, greatly enhanced the importance of lignites, both as fuels and as the raw materials for the manufacture of motor spirit, fuel oils, waxes, &c., by low temperature distillation processes, the carbonaceous residue from which may be briquetted after admixture with a pitch 'binder.' Freshly-mined lignites may contain up to 50 p.c. of water, which, on air-drying, is usually reduced to between 10 and 20 p.c.: many varieties, when completely dried, crumble to powder, which, however, may be again consolidated into a serviceable block fuel by pressure. The ash content usually varies between 5 and 15 p.c., but may run considerably higher. The composition of the dry 'ashless' fuel varies between the following limits: C=60–75, H=5, O=19–34, N=0·5–1·5 p.c., and it has a calorific value of 6000–7000 K.C.Us. per kilog. Lignite burns with a very long smoky flame, and is generally non-caking (*i.e.* it does not yield a coherent coke); it is largely used in Germany and Austria for firing boilers, and for the heating of evaporating pans, the better qualities being sometimes used for metallurgical purposes. Like peat, it may be gasified in producers. W. A. Bone has described a heat treatment of dry lignites and brown coals at temperatures below 400° C. whereby a considerable condensation in their cellulosic or humic constituents may be effected, with simultaneous elimination of H_2O and CO_2, but without any expulsion of either H or hydrocarbons, which may be employed to enhance their fuel values (Proc. Royal Soc. 1921, A. 99. p. 236).

Bituminous coal. This term is applied to a whole series of 'flaming' coals of Primary or Mesozoic origin, and it includes all the economically important coals except anthracites. More than 90 p.c. of the world's total output of 1250 million tons of coal in 1913 (including anthracites, but excluding lignites) was due to six countries (United States 562·6, Great Britain 287·4, Germany 191·5, France 40·1, Russia 28·8, and Belgium 22·8 million tons respectively). Taking a series of nine quinquennial averages over the period 1870–1914 inclusive, the output of coal in Great Britain has increased from 121·5 to 268·2 million tons per annum, whilst the annual consumption per head of population has increased from 3·5 to 4·3 tons. It is estimated that the available supplies within 4000 feet of the surface in Great Britain amount to about 580 times her output in 1913.

In 1920 only 229·3 million tons of coal were raised in Great Britain, at an average pithead cost of 34*s.* 1½*d.* per ton, or almost exactly four times the corresponding pre-war figure. The amount of coal raised per person employed at British mines had fallen from 259 tons per annum in 1913 to only 190 tons per annum in 1920.

According to the Report upon the World's Coal Resources issued by the International Geological Congress in 1913, the total possible and probable reserves of coal of all kinds (anthracite, bituminous, and lignites) within 6000 feet of the surface amount to about 6000 times the present total annual consumption. Of these reserves, 6·75 p.c. are anthracites (mainly in China), 52·75 p.c. are bituminous coal, and 40·5 p.c. are sub-bituminous (lignites and Tertiary brown coals). 51·8 p.c. occur in the United States, 16·4 p.c. in Canada, 13·5 p.c. in China, 5·7 p.c. in the then German Empire, 2·6 p.c. in Great Britain, 2·3 p.c. in Siberia, and 2·2 p.c. in Australia. South America and Africa are relatively devoid of coal-fields.

For commercial purposes, bituminous coals are classified according to their suitability, or otherwise, for certain specific economic ends, *e.g.* steam raising, furnace firing, gas making, manufacture of dense metallurgical coke, and the like. The usefulness of any given coal for a particular purpose depends principally upon (1) its content of 'volatiles' expelled at 900°–1000°, which largely determines the length and character of the flame emitted during vigorous combustion; and (2) the character of the carbonaceous residue after the 'volatiles' have been expelled at high temperature, which doubtless in part depends upon the nature and mode of decomposition of a certain 'cementing' constituent of the coal, and partly also upon the character (fusibility) of the mineral ash associated with it. For economic purposes, Percy proposed to class bituminous coals as (1) non-caking, free burning, rich in O; (2) caking; and (3) non-caking, rich in C. Several classifications have been proposed based upon the ultimate composition of the dry and ashless coals. One of the most useful is that generally attributed to the French metallurgist Grüner, but in reality due originally to Regnault. In a modernised form it is as the table on p. 256.

Some authorities regard the Regnault-Grüner classification as defective, in that it is based chiefly on the 'oxygen' content of the coal, which bears all the analytical errors, and also in that it underrates the importance of hydrogen. C. A. Seyler, as the result of a special study of the coals of South Wales, has proposed a chemical classification based upon the percentages of carbon and hydrogen in the pure coal substance, and dependent on (1) the hydrogen content, and (2) the C/H ratio, as follows:—

Genus	P.c. H	Ratio C/H
1. Anthracitic . .	under 4·0	over 22·0
2. Carbonaceous .	4·0–4·5	20·3–23·35
3. Semi-bituminous .	4·5–5·0	16·6–20·4
4. Bituminous . .	5·0–5·8	14·6–18·2
5. Perbituminous .	over 5·8	12·9–14·7

The U.S. Geological Survey, independently of Seyler's work, have also adopted the C/H ratio as the best available basis for the purpose of scientific

THE REGNAULT-GRÜNER CLASSIFICATION OF COALS (AS REVISED BY THE AUTHOR).

Genus	Class	Chief uses	Percentage composition			P.c. volatiles at 900° C.	P.c. fixed carbon	Character of carbonaceous residue
			C	H	O+N+S			
A. Lignites	Non-caking	—	60 to 75	about 5·0	20 to 35	above 45	below 55	Non-coherent
B. Bituminous	[1] Non-caking long flame	Reverberatory furnaces	75 to 80	4·5 to 5·5	15 to 20	40 to 45	55 to 60	Non-coherent
	[2] Caking long flame	Gas-making	80 to 85	about 5·6	10 to 15	32 to 40	60 to ·68	Very porous coke
	[3] Hard coking	Coke manufacture	84 to 89	5·0 to 5·6	5·5 to 11·0	26 to 32	68 to 74	Dense coke
	[4] Hard coking short flame	Coke manufacture and Steam raising	88 to 90	4·5 to 5·5	5·5 to 6·5	18 to 26	74 to 82	Very dense coke
B.C. Semi-bituminous	Non-caking short flame	Steam raising	90 to 92	4·0 to 4·5	4·0 to 5·5	15 to 20	80 to 85	Weakly caking or non-coherent
C. Anthracitic and Anthracites	[1] Anthracitic non-caking	Steam raising	92 to 94	3·0 to 4·0	3·0 to 4·5	8 to 15	85 to 92	Pulverulent
	[2] Anthracites non-caking	Domestic and central heating; malting kilns				below 8	above 92	

All the numerical data in the above table refer to the dry ashless coal.

classification. It is, however, clear that, pending a much fuller knowledge than we now possess respecting the proximate constituents of coal, neither of the above classifications can be considered satisfactory in any final sense.

In the selection of a coal for any particular purpose, the following points should be borne in mind: (1) the best '*gas coals*' are those in which the ratio O : H is approximately 2 : 0; they yield from 30 to 38 p.c. 'volatiles' (reckoned on the dry ashless coal), and a fairly porous coke of no great strength; (2) the best '*coking coals*' usually yield between 20 and 30 p.c. of 'volatiles,' and are strongly caking; the best '*steam coals*' yield less than 20 p.c. of volatiles, are, as a rule, non-caking and smokeless, or nearly so in their combustion; (4) for '*gas-producer*' purposes it is desirable that a coal should be non-caking, and have an infusible ash. The caking properties of a coal depend upon its containing certain organic compounds (extractable by means of pyridine) which decompose when heated, yielding 'volatiles' and a small amount of a pitch-like cement which acts as a binding material in the resultant coke; *ceteris paribus*, a caking coal with a fusible ferruginous ash will yield a stronger coke than one of similar age and composition with a highly silicious ash. Non-caking or feebly caking coals are either (1) those of greatest age, high in carbon and low both in oxygen and 'volatiles'; (2) those of comparatively recent origin, with a high oxygen content; or (3) those from '*oxidised*' seams which have at some period been exposed to atmospheric influence. Variations in the thickness of the overlying strata seem to influence the coking properties of a weakly caking coal-seam. For coking purposes, it is often advantageous to mix a weakly caking, short-flame coal, rich in carbon, with one which cakes well but yields much gas. Finally, it should be observed, that a caking coal loses its coking properties on prolonged exposure to the atmosphere.

Besides the elements already referred to, coal (ashless) contains two others of importance, viz. nitrogen and sulphur. The nitrogen, although present to an extent of between 1 and 2 p.c. only, is of great economic value, since it is the source of 95 p.c. of the world's entire output of ammonium salts. As the results of exhaustive tests upon some 80 Scottish coals (N=0·915–1·873 p.c.) at the Provan Gasworks, Glasgow, it has been found that under the conditions prevailing during distillation in a modern gas retort, about 58·3 p.c. of the total nitrogen remains in the coke, 19·5 p.c. appears as N in the gas, 17·1 p.c. is obtained as ammonia, 3·9 p.c. passes as organic bases into the tar, and, finally, 1·2 p.c. is evolved as cyano- compounds. Also, as the results of coking a Durham coal containing 1·57 p.c. N in Otto Hilgenstock ovens at Blayden-on-Tyne, A. Short (J. Soc. Chem. Ind. 1907, 581) found that 43·31 p.c. of the N remained in the coke, 15·16 p.c. was recovered as NH_3, 2·98 p.c. appeared in the tar, 1·43 p.c. as cyano compounds, the remaining 37·12 p.c. representing N in the gas. The temperature at which the evolution of ammonia begins when coal is heated seems to depend on its geological age. Carrick-Anderson, and Roberts (J. Soc. Chem. Ind. 1899, 1099) give 333° as the lowest temperature for NH_3 evolution from a young gas coal, and state that with coal of an older type it may rise to about 480°. Hilgenstock has found that the principal evolution of NH_3 occurs after the caking stage of the distillation has set in. M. G. Christie (Inaug. Diss. Aachen, 1908), in an investigation upon peat, gas coals, and anthracites, has shown that evolution of NH_3 begins at about 350° in the case of a gas coal, and at 450° in the case of anthracites, and that the principal evolution occurs between 500° and 700°; according to Christie, also, that part of the N which remains in the coke is present in an extraordinary stable 'nitride' form, and is only slowly expelled as the temperature is raised from 900° to 1900°. From this it would appear that the N is present in at least two distinct forms, viz. (i.) as organic compounds which decompose at a temperature below 900°, and (ii.) in a stable 'nitride' form. Harger (J. Soc. Chem. Ind. 1914, 389) has suggested that the 'ammonia-yielding' N exists in a side chain in the parent molecule, whilst the more stable 'fixed nitrogen' is present in some ring formation.

Sulphur must always be considered as a deleterious element in coal; it appears in three forms, namely, (i.) as pyrites FeS_2; (ii.) as sulphates (gypsum); and (iii.) as '*organic*' sulphur. Although partly expelled (chiefly as H_2S, CS_2, and thiophen) on distillation, the sulphur is largely retained (chiefly as FeS and CaS) in the coke; it is impossible to produce a coke low in sulphur from a coal whose ash is rich in Fe, Ca, or Mg compounds. According to A. Short (*l.c.*), in caking a Durham coal containing 0·824 p.c. S, in by-product ovens, 72·5 p.c. of the S remained in the coke, 24·0 p.c. was evolved as H_2S, 1·45 p.c. passed into the tar, the remaining 2 p.c. being accounted for as gaseous products other than H_2S.

Coal, when freshly mined, may contain much water ('pit water') and some occluded gas. Most of the water is rapidly lost on air drying, whilst the remainder (usually some 2–3 p.c.) is completely lost at 105°. The occluded gas may be withdrawn by continued exhaustion at the ordinary temperature; from a Durham coal (Hutton seam) Bedson obtained 1·6 c.c. of gas per gram of coal; the gas contained CO_2=4·35, CH_4=71·15, C_2H_6=6·65, O=2·80, and N =15·05 p.c. From a Lancashire coal (Lower Mountain Mine), R. V. Wheeler obtained 1·375 c.c. of gas per gram, containing NH_3=0·5, H_2S=0·5, C_2H_4=0·4, CO=2·1, C_2H_6=8·10, CH_4=80·35, O=0·4, and N=7·65 p.c.

The mineral ash in coal varies greatly in amount, colour, composition, and fusibility. A distinction must be drawn between the heavier mineral matter, 'dirt' (pyrites sp.gr. 5·0, shale sp.gr. 2·5, and gypsum sp.gr. 2·3), often mixed with freshly mined small coal (sp.gr. 1·2–1·3) from which a separation can be effected by mechanical washing, and the true or 'fixed' ash of the coal, which is disseminated throughout its entire mass, and cannot be so removed. A pure white ash which the writer once obtained from an Australian coal contained 53·4SiO_2, 44·0Al_2O_3, together with some 2 p.c. only of lime and the merest traces of ferric oxide. Usually the ashes of coals contain, in addition to Al_2O_3 and SiO_2, variable proportions of CaO, MgO, Fe_2O_3, and SO_3 (chiefly as $CaSO_4$); the colour varies from cream or light-buff to red-brown, according to the iron content, and, as a rule, the fusibility increases with the darkening colour. The ashes of a typical Lancashire coal will contain SiO_2=25–40, Al_2O_3=19–28, Fe_2O_3=22–32, CaO=3–16, MgO up to 3·5, and SO_3=3–8 p.c. A fusible ferruginous ash is a constant and prolific source of clinkering troubles in furnaces and gas producers. According to J. T. Dunn the melting-point of a coal ash may vary between 1000° and 1500° C. (or even higher) according to its chemical composition; and, although no general law can yet be formulated, the m.p. usually rises as the relative total *molecular* proportion of basic oxides to silica diminishes (Journ. Soc. Chem. Ind. 1918, 37, p. 171).

Whilst the majority of organic solvents (ether, alcohol, chloroform, benzene) have but little effect upon coal, Bedson has called attention to the remarkable solvent action of pyridine (b.p. 114·5°) (J. Soc. Chem. Ind. 1908, 27, 147). The coal should be ground so as to pass through a sieve of 1000 apertures per sq. in., then mixed with sand and extracted with the solvent in a Soxhlet apparatus. The residual carbonaceous material is always quite devoid of coking properties.

The pyridine solutions so obtained are dark brown in colour, with sometimes a green fluorescence, and the proportion of the coal substances extracted ranges from practically zero in the case of anthracites up to between 35 and 40 p.c. in the case of a good gas coal. The extract remaining after the solvent has been drawn off is a chocolate-brown amorphous solid, which on ignition decomposes with intumescence, yielding a large proportion of 'volatiles,' and a swollen residue of coke. From Bone and Sarjant's researches it would appear that in order to obtain any reliable results with a series of coals by the Soxhlet extraction method, attention must be paid to the purity of the pyridine, and especially to its being anhydrous, and that the whole operation should be carried out in an inert atmosphere of nitrogen. Other organic bases, such as aniline (b.p. 184°) and quinoline (b.p. 238°) have a similar solvent action to pyridine, and in general the higher the b.p. the greater and more rapid the action. Phenol also will extract (at 100°) considerable proportions of the coal substances. Mention should also be made of the recent work of F. Fischer and W. Gluud upon the solvent action of benzene upon coals at temperatures and pressures (288° and 50 atmos.) approximating to the critical constants of the solvent.

The work of R. V. Wheeler and Burgess upon the volatile constituents of coal (Chem. Soc. Trans. 1910, 97, 1918; 1911, 99, 649; 1914, 105, 131) has thrown an interesting light upon the chemical nature of coal. The behaviour of anthracitic, semi-bituminous, and bituminous coals at definite temperatures between 100° and 1100° was carefully investigated; it has been established (1) that 'occluded' gases, mainly higher paraffins, are evolved in small quantities up to 150° or even 200°; (2) that there is a copious evolution of water ('water of constitution') beginning at about 200° and continuing up to, and probably beyond, 450°; (3) that between 270° and 300° H_2S is freely evolved, after which olefines (higher than C_2H_4) appear up to 350°; (4) that a 'critical point' is reached about 350°, which is marked by a rapid increase in the gas evolution and the appearance of much viscous oil; (5) that up to 450° or 500° higher paraffins, C_2H_6, C_3H_8, C_4H_{10}, &c., as well as methane, are conspicuous decomposition products, whereas H is produced in very small quantity; (6) that the evolution of paraffins ceases entirely at about 700°, the absolute amount of CH_4 reaching a maximum at 800°–900°; and (7) that between 700° and 800° there is a 'critical point' above which the evolution of H abruptly and rapidly increases. It has been shown by D. T. Jones and Wheeler, Pictet and Bouvier, as well as by Bone and his collaborators, that the low-temperature tars obtained on distilling coal up to temperatures of 500° or 600° consist chiefly of hydrocarbons of the naphthene (C_nH_{2n}) and hydroaromatic series, together with some paraffins, but not benzene or its homologues. Certain hydroxy compounds, such as hexahydro-*p*-cresol $C_7H_{14}O$, as well as a series of homologous phenolic bodies, including $C_8H_{10}O$ (b.p. 185°–190°), $C_9H_{12}O$ (b.p. 198°–200°), $C_{10}H_{14}O$ (b.p. 213°–215°), and $C_{11}H_{16}O$ (b.p. 226°–228°) have been identified in such low-temperature tars. The results of a large number of investigations carried out in recent years by British, French, and American chemists all point to the conclusion that the 'ash free' coal substance is a conglomerate of (*a*) cellulosic degradation products, (*b*) nitrogenous compounds of vegetable proteid origin, and (*c*) resinic bodies derived from gums, waxes, resins, &c., in the original vegetable *débris* from which the coal was formed. Up to recently, it has generally been supposed that the coking propensities of coals are mainly due to their resinic constituents; but this has been disproved by Bone and co-workers, who have shown that the main cause of coking are certain types of humic bodies whose softening or melting points lie below the temperature at which active decomposition sets in. For a complete discussion of the chemistry of coal, *vide* 'Coal and its Scientific Uses,' by W. A. Bone (1918).

When bituminous coal is charged into a hot furnace, it first of all undergoes a process of destructive distillation; its least stable resinous constituents decompose, and hydrocarbons are freely evolved, which, on partial oxidation or secondary decomposition, give rise to carbon, together with minute quantities of dense tarry vapours (smoke) which are difficult to burn, except in an abundant air supply and at high temperatures. The residual 'semi-carbonised' fuel, being raised to incandescence, is burnt by the air, which is drawn in through the grate. If, as in intermittent stoking, the furnace be cooled by a sudden inrush of cold air during the introduction of a fresh charge of fuel, smoke will be freely evolved. The production of smoke may be greatly reduced by the adoption of continuous mechanical stoking, especially if it be on the 'under-feed' principle, or by making the mixture of 'smoke' and *hot* air impinge upon an incandescent fireclay surface; the introduction of a pre-heated secondary air supply near or at the fire-bridge of the furnace will often diminish smoke. It is never possible to burn coal in a furnace with the theoretical quantity of air; thus 1 lb. of coal containing C=80·0, H=5·5, S=0·9, N=1·5, O=5·0, and ash =7·0 p.c., would, theoretically, require 136·0 cub. ft. of dry air at 15° and 760 mm. for complete combustion, and the cooled gaseous products would contain 18·2 p.c. CO_2. It rarely happens, however, that the CO_2 content in the cooled chimney gases from a coal-fired furnace exceeds 13·0 p.c., and the more usual proportion is from 8·0 to 10·0 p.c. In large boiler installations, the adoption of mechanical stoking, together with automatic instruments for recording the temperature and CO_2 content of the chimney gases, will be found conducive to fuel economy. E. J. Constam and P. Schlapfer of the Zurich Prüfungsanstalt für Brennstoff, as the result of exhaustive boiler trials with many different coals, conclude that those yielding between 16 and 23 p.c. of 'volatiles' (referred to dry ashless fuel) have the greatest steam-raising values; with coals yielding a high percentage of 'volatiles,' there is an excessive loss on account of their incomplete combustion; whilst, on the other hand, with a coal low in 'volatiles,' and which, therefore, yields a large percentage of coke in the boiler furnace, a considerable excess of air must be used in order to maintain combustion at a rate sufficient to ensure rapid evaporation in the boiler, and this means an excessive loss as sensible heat of the chimney gases. In trials on a marine boiler with coals yielding between 16·5 and 19·1 p.c. 'volatiles,' evaporating about 3·6 lbs. of water per sq. ft. of heating surface per hour, between 73·7 and 75·1 p.c. of the heat of combustion of the fuel was transmitted to the water, about 20 p.c. was lost in the chimney gases (at 276°–303°), partly as sensible heat and partly as unburnt gases, another 3–3·4 p.c. was lost in the ashes, the balance representing radiation losses (Zeit. des Ver. deut. Ingenieure, 1909, 1857). In trials on a goods locomotive on the Furness Railway, fired with Yorkshire, Lancashire, Cumberland, Scotch, and Welsh coals, the average boiler efficiency reported was 74·5 p.c. for an average evaporation of 8·65 lbs. of water per sq. ft. of heating surface (Pettigrew, Jour. Iron and Steel Inst. 1903, ii. 206). In coal-fired Lancashire boilers the efficiency realised rarely exceeds 70 p.c., and is sometimes much lower.

Anthracite is the ultimate product of the conversion of vegetable matter into coal. Its average composition is 91·29 C, 2·91 H, 2·75 O+N, 3·05 ash. The percentage of N varies from 0·58 to 2·85; that of sulphur from 0·63 to 1·0. Anthracite is hard and brittle; it has a sub-metallic lustre, a conchoidal fracture, and a sp.gr. of 1·35–1·7. It burns with a smokeless flame. Some varieties (*e.g.* Welsh anthracites) decrepitate considerably, even when gradually heated. This property is not exhibited by the anthracites of Pennsylvania.

2. *Carbonised Fuels.*

Wood charcoal. When wood is heated to 200° without access of air, it remains unaltered, at 220° it becomes brown, and at 270°–300° it suffers decomposition, torrefied wood or *Rothholz* being formed. At 350° it is resolved into volatile products and a fixed residue of charcoal. Good charcoal produced at 350°–400° is porous, black, sonorous when struck, has a conchoidal fracture and a ligneous texture. It burns without smoke, and in separate pieces without flame. Its sp.gr., exclusive of pores, is 1·5–2; inclusive of pores, 0·2–0·35 in soft charcoal, and 0·35–0·5 in hard. Dry charcoal contains on an average 90 C, 3 H, and 7 O. After storing, it contains 70·45 C, 1·68 H, 13·1 O, 1 ash, 13·76 moisture and gases. The usual percentage of ash is 3–4. The carbonisation or dry distillation of the wood may be effected in the open air in circular piles or stacks (Meiler), provided with a yielding cover; in rectangular piles; in pits (the most primitive method); in kilns of brick or stone; or in iron retorts heated externally (method used in the manufacture of gunpowder and of pyroligneous acid). The yield of charcoal varies with the nature, age, and condition of the wood, and with the method of carbonisation, from 31 p.c. by volume (branchwood of fir) to 80 (logs of the same). In Sweden, 67 p.c. of the volume of the wood was obtained in piles in which the wood was stacked vertically, and 75 when stacked horizontally. The yield by weight ranges from 15 to 28 p.c. The more slowly the charring is effected, the greater will be the yield of charcoal. Charcoal is an excellent fuel for metallurgical purposes on account of its low percentage of ash and its high calorific power.

Peat charcoal is very friable and porous, and consequently difficult to use in metallurgical operations. When sufficiently coherent, and when the percentage of P_2O_5 is low, it may be used in low, small furnaces. The carbonisation may be effected in open kilns, in pits, or in ovens in which the air for combustion passes from above downwards, or by external firing in closed vessels, in order to enable the volatile products of distillation to be collected. Peat charcoal is easily kindled, and has a calorific power of 6500–7000 cals. It is not adapted for iron making, but may be used advantageously for gas furnaces, on account of the large size of the lumps, absence of clinker, and the fact that the ash readily falls through the bars.

Coke is the solid product of the carbonisation of coal. It varies considerably in external character. For metallurgical purposes, the best coke is compact, heavy, homogeneous, with bright light-grey surface. It contains, besides carbon and ash, small quantities of hydrogen (0·2–1·2 p.c.), oxygen (traces and up to 8 p.c.), nitrogen (0·4–1·5 p.c.), and 'organic' sulphur (total S=0·8–1·8 p.c.). The best cokes contain upwards of 90 p.c. C, and less than 8 p.c. ash, and should have a metallic ring. Coke is only slightly hygroscopic, and when thoroughly dried does not absorb more than 1–2 p.c. of moisture from moist air. The moisture in coke put on the market should not exceed 3 p.c. The calorific value of dry coke containing 90 p.c. C and 0·5 p.c. H is about 7450 K.C.U. per kilog. (*cf.* COKE MANUFACTURE).

Semi-Coke (coalite) is the name given to the carbonaceous residue got by carbonising a gas coal at low temperatures (450°–600°). Various attempts have been made within recent years to manufacture in this way a satisfactory smokeless fuel for domestic use, the chief difficulty being to produce on a large enough scale, and at a price comparable with that of raw coal, a fuel capable of being economically transported by rail. Attempts have been made to overcome this difficulty by either compressing the product whilst it is still hot and in a pasty or intumescent condition, or by briquetting it with a suitable binder. A complete solution of the low-temperature distillation problem would not only be the best and most economical means of abolishing the domestic smoke nuisance, but would also make available large quantities of motor spirit and fuel oils for commercial and naval purposes. Laboratory tests upon typical British bituminous coals have shown that on carbonisation at 550° to 600° C. they will yield 10 to 15 per cent. of their weight of motor spirit and fuel oil, as well as 3000 to 4000 cub. ft. per ton of rich gas. Also, it has been proved that the resulting semi-coke burns with so high a radiant efficiency in domestic fireplaces that it would probably constitute the cheapest medium of heating living-rooms by 'radiation' (*vide* W. A. Bone, Proc. Mech. Eng. 1921, p. 625).*

3. *Compressed Fuels.*

Patent fuel (briquettes). Numerous patents have been taken out for producing a good fuel by mixing various substances with small coal in proportions sufficient to enable the mixture to be pressed into a coherent block. Various binding materials have been tried, *e.g.* soluble glass, asphalt, pitch, and turpentine. Meal made from potatoes was abandoned because the blocks were not water-tight. Coal tar (Warlick's process) was tried at Swansea, the blocks being baked after compression, whereby a quantity of tar was recovered. On the Continent, cellulose (D. R. P. 7590, 1879) and treacle (D. R. P. 31715, 1884) have been tried. Pitch made from coal tar has been used for many years with great success. Two modes of manufacture are in vogue in South Wales. In the dry process, small coal is carried by an elevator into a large bunker, whence it is lifted by another elevator to a shoot into which it is tipped with the contents of a small elevator containing pitch. The mixture then passes into a Carr's disintegrator, and the resulting product, containing 8–12 p.c. of pitch, passes to heaters, and finally to the presses, which turn out 100–200 blocks, weighing 10–30 lbs. per day of 12 hours. In the steam process, there is used a large vertical iron cylinder with arms revolving inside, constantly kept full of the mixture of pitch and coal. High-pressure steam is injected near the bottom, and allowed to percolate up through the mass, whilst the arms expose every portion to its action. Mixtures such as these described are also compressed into small ovoid briquettes of various sizes, suitable for domestic use or steam-raising purposes on boilers fitted with mechanical chain grates. Attempts have been made to utilise peat by mixing it in a state of powder with small coal and sawdust, and pressing the mixture into blocks. Also dried lignites, or the non-coherent carbonaceous residues obtained by carbonising them at low temperatures, may be successfully briquetted with the addition of pitch as a binder. According to tests carried out by the staff of the U.S. Geol. Survey in 1904, it is possible to make good briquettes from a strongly coking coal, heated until intumescence just begins, and immediately afterwards pressed, without the addition of any binding agent. Anthracite culm or coke breeze may be briquetted without the addition of any bituminous coal, provided that good pitch be used as a binding agent. The pitch should be anhydrous, or nearly so, and should contain a certain proportion (7–11 p.c.) of creosote oils distilling below 215°, to give it good binding properties; the presence of free carbon in any quantity is objectionable, and the pitch should not flow below 70°. A good quality of powdered coal with 6 p.c. of pitch should yield a clean hard briquette, which will not disintegrate in the fire. In many cases briquetted coal will stand transportation better than the original coal, and is as good or even better as a steam-raising fuel.

The pre-war cost of briquetting coal in this country (including capital charges) was between 2*s.* 6*d.* and 3*s.* per ton. The world's production of briquettes amounted to upwards of 30 million tons, of which nearly three-fourths were made in Germany.

Literature.—E. Preissig, Presskohlenindustrie, Freiberg, 1887; Report of Coal Testing Plant of U.S. Geol. Survey, iii. 1904; A Handbook of Briquetting, G. Franke (Berlin), translated by F. C. A. H. Lantsberry, 2 vols. (Griffin & Co., London), 1916–1918.

4. *Powdered Fuels.*

It is well known that a mixture of coal dust and air is highly explosive, and in burning coal the excess of air actually required diminishes with the fineness of division of the fuel. The efficiency of the combustion approaches the theoretical maximum the more nearly the system attains to the homogeneity of a properly proportioned gas-air mixture. Much progress has been made in recent years in applying powdered coal to boilers and metallurgical furnaces. As long ago as 1873 Crampton (Jour. Iron and Steel Inst. 1873, 91) worked out a system whereby pulverised coal was fed into furnaces through an injector type of burner, air being supplied in measured quantities by a fan, so that intense heat was generated. In recent years the system has been largely applied in America to cement kilns, reverberatory and open-hearth furnaces, with considerable success, and it is also being developed in connection with boiler-firing. According to Canadian experience, the following conditions are essential for obtaining the best results: (1) that the coal shall be dried so that its moisture content is less than 1 p.c. before being pulverised; (2) that it shall be pulverised until 85 p.c. of it passes through a 200 mesh, and 95 p.c. of it through a 100 mesh; (3) that the furnace shall be properly shaped and proportioned, and be suitably equipped with burner and feeding arrangements so that the relative deliveries of coal dust and air can be well controlled, and that special provision shall be made for the periodic removal of ashes from the flues at the far end of the furnace. In regard to steam-raising, special mention should be made of the use of pulverised coal in the Bettington boiler, which has been successfully developed in this country and in S. Africa. For particulars of recent developments of pulverised coal systems in America *vide* The Fuel Research Board's Special Report, No. 1 (1919), by L. C. Harvey.

Valuation of coals. Whilst the value of coal as a fuel depends primarily upon its calorific value, other factors must be considered in determining its suitability for any given purpose, as, for instance, (1) moisture content; (2) quantity and fusibility of ash; (3) percentage of 'volatiles' and the character of the coke residue; (4) ultimate analysis C, H, S, and N—the N being important if the coal is to be carbonised or gasified in producers under ammonia-recovery conditions. Coal is rarely purchased in Great Britain subject to either chemical analysis or calorific test, but the practice is common in the United States and in certain European countries, the contract, in any particular case, naming a certain price for a coal of specified quality, subject to a sliding scale for variations in quality within certain defined limits. In sampling a consignment of coal for assay purposes, special care should be taken that the sample truly represents the bulk; the method adopted will obviously depend somewhat on circumstances, but the sample should contain the same proportions of large, medium, and small coal as the bulk, and, as a rule, should weigh not less than 1 cwt. On reaching the laboratory the whole should be put through a crusher and subsequently reduced to convenient bulk by successive 'quartering'; the final sample should then be further crushed to coarse powder and stored away in air-tight tins. The chemical tests may be carried out as follows: (1) *Moisture and ash.* 10 grams of sample, in a weighed porcelain basin, are dried in an oven at 105° for 1 hour, and subsequently incinerated in a muffle at bright red heat, care being taken that the initial 'distillation' is not too rapid. The colour of the ash should be recorded, and observation made as to its fusibility. (2) *Volatile matter.* The method recommended by a committee of the American Chemical Society is to determine loss in weight when 1 gram of the dry sample is heated in a covered platinum crucible of 30 c.c. capacity for 7 minutes over the full flame of a Bunsen burner, screened from draughts by a cylindrical asbestos chimney. A more useful test, however, is the 'crucible coke assay,' in which 20 grams of the dried sample are carbonised in a fire-clay crucible (lid on) at 900°–1000° in a muffle furnace; the heating is continued for 5–10 minutes after the flame, caused by the volatile matter burning at small holes in the crucible lid, has completely died away. A new method, capable of giving more accurate results of scientific as well as of commercial value, has been described by Bone and Silver (Trans. Chem. Soc. 1921, 119, 1145); also another improved method has been proposed by Lessing (J. Soc. Chem. Ind. 1912, 31, 465).

(3) *Ultimate analysis for C and H.* This may be carried out on a dried sample (0·2 gram) by the 'combustion' method ordinarily employed in the case of organic compounds, the combustion tube being packed with granular lead chromate. (4) *Sulphur.* (*a*) About 2 grams of the sample are ignited with three times its weight of a mixture of 2 parts MgO and 1 part pure anhyd. Na_2CO_3 in a porcelain dish or large crucible for 1½ hours in a muffle furnace (preferably electrically heated). Afterwards the charge is washed into a beaker, excess of dil. HCl *plus* bromine water is added, and after boiling off the excess of bromine, the contents of the vessel are vigorously stirred and then filtered. The sulphate in the filtrate is then precipitated with a slight excess of $Ba(NO_3)_2$, and finally estimated as $BaSO_4$ in the usual manner. Determinations are made in triplicate, and a blank experiment is always simultaneously performed in order to determine the 'correction' to be applied on account of any traces of sulphate in the reagents employed or the fixation of SO_2 by them from the furnace gases. (*b*) In determining the sulphur in the *ash* of a coal, it is fused in a platinum crucible with an excess of Na_2CO_3 and K_2CO_3 mixture *plus* KNO_3 in order to convert all sulphur compounds into soluble sulphates. The fused mass is subsequently extracted with excess of hot dil. HCl, and the extracted sulphates determined as $BaSO_4$ in the usual way. (5) *Nitrogen* is best determined by the ordinary Kjeldahl method. Occasionally coal or coke must be examined for *arsenic*. (For details of the method recommended by the committee appointed by the Board of Inland Revenue, *see* T. E. Thorpe, Estimation of Arsenic in Fuel (Chem. Soc. Trans. 1903, 83, 969).)

Storage and spontaneous ignition of coal. It is well known that on storage coal deteriorates both as regards heating power and coking properties, a fact attributable to slow atmospheric oxidation, which may, in certain circumstances, give rise to spontaneous ignition of the coal. It was formerly believed that the oxidation of the iron pyrites present in coal is the principal cause of its spontaneous ignition, but it is now recognised that this is not so, the chief factor being the surface condensation of oxygen in the pores of the fuel, and subsequent oxidation of certain constituents of the coal substance. It has also been suggested, on the basis of experimental evidence, that in some cases of spontaneous combustion, the heat generated by bacterial activity is a factor to be considered. Coal readily absorbs oxygen when heated in contact with air at 150°–200°, the process being not merely a physical absorption, but involving actual oxidation of coal substance; the weight first of all increases, and afterwards, especially if the temperature rises, steadily decreases owing to loss of moisture, slow combustion, and decomposition. According to investigations by S. W. Parr and F. W. Cressman, of the University of Illinois, the oxidation of coal is continuous over a wide range of conditions, and begins with freshly mined coal at ordinary temperatures; at some temperatures between 200° and 275° (dependent upon the nature of the coal and the fineness of division) the oxidation becomes autogenous; actual ignition does not occur until the temperature rises beyond 350°. With regard to the influence of pyrites, it was found that the amount of 'pyritic oxidation' under given conditions is always proportionate to the pyritic content of the coal, so that an increase in the latter may therefore hasten 'the rise in temperature up to the critical point at which the absorption of O by the coal itself is rapid enough to increase the temperature up to the point of self-ignition.' Hence, pyritic oxidation may become a contributory (though not the chief) factor in the spontaneous ignition of coal, although *by itself*, and apart from the simultaneous oxidation of the coal substance, it would be a negligible one. According to Parr and Cressman, the presence of moisture increases the reactivity of the coal-air system at any temperature. The whole phenomenon is probably one of 'surface combustion.' According to Bone's investigations the absorption of O by typical British (Durham and Yorks.) bituminous coals is very slow at temperatures below 80°, and is unattended by the production of relatively insignificant quantities of the oxides of carbon. But in the neighbourhood of 80° the action becomes much quicker, and at above 100° is marked by the regular and simultaneous production of both the oxides of carbon as well as steam, all of which apparently result from the decomposition of some unstable 'oxygenated' body primarily formed by the absorption of the oxygen. An important official report upon The Spontaneous Combustion of Coal in Mines, containing a full account of recent researches by R. V. Wheeler and others, has recently been issued (Cmd. 1417 of 1921). With regard to the storage of coal, it has been proved that coal stored *under water* suffers no deterioration. The conditions most favourable to spontaneous ignition of coal when stored in heaps are (1) a certain, but not excessive, ventilation of the heap; (2) a certain degree of subdivision (*e.g.* small coal mixed with dust); and (3) any circumstance which tends to heat conservation in the heap. The best safeguard is either excessive ventilation (which it is practically impossible to maintain in large stores or in a ship's hold) or no ventilation at all. The extinction of fires which may break out on board ship is often a matter of great difficulty, the most effective method being that recently proposed by Harker, whereby the flue gases from the boilers of the vessel are pumped into the burning hold.

British coal-fields. The coal-fields of Great Britain may be grouped in three principal areas, each having distinctive features, namely: (*a*) *Southern* (S. Wales, Forest of Dean, Somerset, and Dover); (*b*) *Central* (Yorkshire, Lancashire, Derbyshire, N. Wales, and Midland Counties); and (*c*) *Northern* (Scotland, Northumberland, Durham, and Cumberland). The more important fields are as follows:—

(1) *South Wales* (Monmouth, Glamorgan, Carmarthen, and Pembrokeshire), covering an area of 850 sq. miles, of which 150 are under the sea, with seams 1–12 feet (average 2·5–3·0 feet) thick, and yielding all classes of coal, bituminous (31 p.c.), steam coals (47 p.c.), and anthracites (22 p.c.). The carboniferous strata lie in an elongated basin, which is almost com-

pletely surrounded by older formations, and complicated towards the south by an anticlinal fold running east and west. The basin is much faulted, and the rivers have cut a series of deep valleys along which the coal seams crop out. Speaking generally, and for corresponding depths below the surface, there is a gradual transition in the character of the coal from the coking varieties in the east, through the first-class steam coals of the centre, to the semi-anthracites and anthracites in the west; moreover, the seams have apparently been subjected to an increasing earth pressure in the direction east to west, a circumstance which may account for their increasing anthracitic character. This supposition has been disputed by Strahan and Pollard (Memoirs of the Geological Survey, 1908), who, from the fact that the ash content of the anthracites is invariably much lower than that of the neighbouring bituminous seams, argue that the difference between the two classes of coals must be due to some difference in the original vegetable *débris* from which they have been derived. In the east section of the field the upper and middle coal-measures are worked, yielding good coking and bituminous coals; in the centre the middle measures predominate, the upper being found in patches only; whilst in the extreme west the lower measures only are found. The composition of the more important classes of coals usually falls within the following limits:—

Class	C	H	O and N	S	Ash	Volatiles
Anthracites . .	91·0–93·0	3·0–3·7	1·9–3·5	0·7–1·0	0·7–1·7	5·0–6·0
Steam . . .	85·0–90·0	4·0–4·7	3·5–4·5	0·7–1·5	2·0–3·3	7·0–20·0
Bituminous (coking)	80·0–95·0	5·0–5·5	—	—	—	20·0–25·0

(2) *Forest of Dean.* A small field (34 sq. miles) between the Wye and Severn valleys, containing 31 seams, of which only 16 exceed 1 foot in thickness. The total thickness of the measure is 2765 feet, and they are completely girdled by older formations. The coals resemble in character those found in the east section of the S. Wales field; the upper and middle measures yield excellent gas and house coals, and the lower measures, which, however, are difficult to work, owing to accumulation of water therein, contain good steam coals. (3) *Bristol* (Somerset and Gloucester). The coal-fields of this region form a number of basins of varying areas (total=2385 sq. miles), the edges and outlines of which are marked by newer rocks, so that there are five or six detached 'exposed' fields and a considerable intervening area of 'concealed' fields. The upper parts of the measures (the Radstock and Farringdon series) yield bituminous house and gas coals; the lower parts (Kingswood and Volster series) yield both house and coking qualities. All these are consumed locally. (4) *Staffordshire*, divided into N. Staffs. (95 sq. miles) and S. Staffs. (150 sq. miles). In the northern area the sequence of upper, middle, and lower measures is complete, although much broken by faults; towards the south the measures thin out considerably in respect of total thickness, but the individual seams converge, finally forming the famous Dudley 10-yards seam: in the extreme south the lower measures become so attenuated that it is doubtful whether they exist at all. The northern area yields good coking as well as gas, house, and furnace coals; in the south coking and steam coals are practically non-existent, but both gas and house coals (chiefly of the Pennant series) are obtained. (5) *Leicestershire* and *Warwickshire.* In Leicestershire the exposed area is about 30 sq. miles, and in Warwickshire about 150 sq. miles; the seams have been subjected to igneous intrusion, and probably also to atmospheric influences, and are generally 'oxidised'; hence the coals are non-coking, with a high percentage of 'volatiles.' (6) *Yorkshire, Derbyshire,* and *Nottingham.* A large area, including some 1328 sq. miles of 'concealed,' and about 808 sq. miles of 'exposed' measures; the upper measures have been proved in boring operations, but they are very thin and of no commercial importance. Throughout the area the sequence of the Carboniferous Formation is complete, the coal-bearing measures being underlaid by the Millstone Grit and the Carboniferous Limestone, and they have nowhere been affected by igneous intrusions. The chief seams belong to the Pennant (middle) series; all seams yield highly bituminous coals, with 25–40 p.c. 'volatiles.' The best house coals are obtained in this field. All the coals found north of Sheffield have marked coking properties, though few of them yield a really first-class coke; south of Sheffield the character of the coal changes, gradually losing its coking properties. Between Mansfield and Nottingham the seams have been 'oxidised,' and although the coal yields a large amount of gas, it is non-coking. (7) *Lancashire.* An irregular area, much faulted and broken by an E.–W. anticline, extending from Burnley in the north to Ashton-on-Lyne in the south (with a long tongue projecting southwards through Stockport to Macclesfield), and from Oldham in the east to St. Helens in the west; total 'exposed' area=500 sq. miles. The principal seams in the southern and central areas of the field are all formed in the middle parts of the measures, the upper parts contain no workable seams. The seams in the lower part of the measures become important in the Accrington and Burnley districts. The coals from seams in the middle parts of the measures belong almost exclusively to the 'gas-coal' class, containing 30–35 p.c. 'volatiles'; several of the seams, notably the Yard Mine, Arley, and Trencherbone, yield a fairly good coking coal. The famous 'Mountain Mine' seams of the lower measures (Burnley and Accrington) yield a coal with 26–27 p.c. 'volatiles,' which produce a coke almost, if not quite, equal to the best Durham coke. (8) *North Wales* (Flints. and Denbighs.). Similar in character to the Lancashire field, but with the upper measures rather more developed.

All the workable seams, however, are in the middle parts of the measures; the seams in the lower parts of the measures are all thin. The coals are similar to those of Lancashire; they contain 33–35 p.c. 'volatiles,' and yield a fair quality of coke. (9) *Durham and Northumberland*. In the great northern coal-field, of which Durham and Northumberland form a part, there is a development of coal-seams (more strongly marked the farther north) in the Carboniferous limestone, a feature which is absent in the Midland and Southern fields. In the Limestone series there are a few workable seams which increase in number and thickness from south to north, but in the main part of the field the coal occurs chiefly in the middle parts of the measures. The total area of the coal-field is 800 sq. miles. The S. and W. districts of Durham produce, perhaps, the finest coking coals in the world, containing 22–28 p.c. 'volatiles,' and low both in sulphur and ash. The central district (Sunderland to Newcastle) produces fine qualities of gas and house coals. The Northumberland seams are, for the most part, 'oxidised'; they contain a rather large amount of moisture, and are non-coking. They are largely used as steam coals, and they are excellent as 'producer' coals. (10) *Cumberland*. The character of the coals is similar to those obtained in N. Durham. (11) *Scotland*. The Scottish coal-fields extend from Fifeshire on the east, across a belt between the Forth and Clyde, and westwards into Lanarkshire and Ayrshire, with an isolated small area in Midlothian. The upper parts of the measures are well developed throughout the area. The middle parts of the measures attain a thickness of from 800 to 1500 feet. Below the latter is the 'edge-coal' group in the Carboniferous Limestone series, highly inclined at its outcrop (Fifeshire, Midlothian), and containing bands of cannel. Generally speaking, the coals are bituminous, with a high percentage of 'volatiles'; the best coking varieties are found in the neighbourhood of Glasgow, and the coking seams stretch as far eastward as the Firth of Forth. The Ayrshire coals are chiefly non-coking, and are excellent as 'producer' coals. In Fifeshire the seams in the Carboniferous limestone in the neighbourhood of Dunfermline yield first-class steam and house coals. The Scottish coal-fields have been subjected to igneous intrusions to an extent rarely met with in England, and, consequently, some of the bituminous seams have been locally converted into steam coals and anthracitic varieties.

German coal-fields. The principal coal-fields formerly included in the German Empire are those of (1) *Upper Silesia* (districts of Ratibor, Beuthen, Zabrze, Konigshütte, Laurahütte, and Pless). The measures are 600 metres deep with seams 3–4 metres thick. The best coking coals are found near Zabrze eastwards, from which they gradually change into young gas coals, near Konigshütte, and finally into non-coking flaming coals near Laurahütte. (2) The *Ruhr basin*, stretching from the neighbourhood of Hamm in the N.E. to the Rhine in the S.W.; the field is much broken by faults, and the older measures, which yield the best coking coals, are, as a rule, uppermost; the middle measures yield gas coals, and the lower measures non-coking varieties. The coals of the Ruhr basin contain 84–97 p.c. of organic matter, of which C=83·1–87·1, and H=5·27–5·68. (3) The *Saar district*; the upper and middle measures are both thin and yield non-coking and flaming coals, the lower measures are thick, and yield (especially the deepest) very good caking and coking coals. The ash in Saar coals varies between 1·5 and 4·5 p.c. as a rule, occasionally running up to 7·7 p.c. The carbon varies between 70 and 84 p.c., and the hydrogen between 4·7 and 5·2 p.c.

American coal-fields. The following information has been abstracted from the comprehensive Report of the U.S. Geological Survey issued in 1906; the chief coal-producing states are arranged in order of their present economic importance, the figures in brackets indicating in each case the output in millions of short tons, for 1904. (1) *Pennsylvania* (73·1 anthracitic and 98 bituminous). The anthracite field lies in the N.E. and the bituminous field in the W.; the latter produces the famous Connellsville coking coals, the almost equally famous Youghioghony gas coals, and numerous grades of steam and domestic coals. (2) *Illinois* (36·5). This state includes the greater part of the eastern interior coal-field, which extends from Rock Island and Wilmington (Ill.) in the north to Central Kentucky in the south and from the Mississippi river in the west to Williamsport and Cannelton (Ind.) in the east. The coals are rather low grade and weakly coking, containing C=54–76, H=4·5–5·3, N=0·8–1·2, S=1·3–4·5, O = 12·0–18·5, and ash = 12·0–24·0 with calorific values 9929–11,907 B.Th.Us. per lb. The proximity of the field to Chicago and St. Louis enhances its economic importance. (3) *West Virginia* (32·6). This state includes a large portion of the important Central Appalachian coal-field, which produces high-grade steam coals also suitable for coking purposes, and containing C=74–86, H=4·0–5·2, N=1·0–1·7, S=0·5–1·2, ash=4·6–11·3, with calorific value 13,736–15,190 B.Th.Us. per lb. (4) *Alabama* (11·26) includes several fields of which the Warrior basin is the most important (23 workable seams), constituting the fuel supply of the Birmingham (Ala.) iron industry. The coal is of fair coking quality, containing C=69–72, H=4·8–5·0, N=1·55–1·66, S=0·7–1·02, ash=12·5–12·6, with calorific value 12,238–12,992 B.Th.Us. per lb. (5) *Indiana* (10·9) includes the eastern section of the Eastern interior coal-field (*vide* Illinois). (6) *Kentucky* (7·5). The eastern part of the state includes part of the Central Appalachian coal-field (*vide* West Virginia) and part of the eastern interior field in the west. Both fields yield good steam and coking coals, the eastern area being in this respect superior to the western; the coke for the western field has too high a S content to be of much use as a metallurgical fuel. (7) *Colorado* (6·65). The most important coal-producing state west of the Mississippi river; the coal is a black lignite, which so rapidly disintegrates on exposure to air, that its transport over any great distance is impossible. It contains C=61·1, H=5·75, N=1·22, S=0·58, O=24·95, ash=6·37, with cal. value 10,546 B.Th.Us. per lb. (8) *Iowa* (6·5) yields only low-grade coals containing high percentages of moisture, sulphur, and ash, with very feeble coking properties.

(9) ***Kansas*** (6·3) yields fairly good non-coking steam coals. (10) *Wyoming* (5·1) contains a number of apparently independent coal-fields in strata of the Cretaceous age; the fuel is low grade. (11) *Indian Territory* (3·04) produces good steam coal, with, in some instances, fair coking properties, but usually high in sulphur. C=63–72, H=4·8–5·2, N=1·4–1·7, S=1·5–4·0, ash=10·0–13·5, with cal. value 11,340–12,874 B.Th.Us. per lb. The coke is good enough for lead smelting, but unsuitable for iron smelting.

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B. Liquid Fuels.

Whilst increasing quantities of hydrocarbon oils (crude petroleum or its distillation products, shale oil, benzol, &c.) are being used as fuel for certain special purposes, they cannot be regarded as a serious competitor of coal or as in any real sense a substitute for it; it is doubtful whether the calorific value of the world's entire output of petroleum and other liquid fuels in any given year exceeds (if, indeed, it is equal to) 5 p.c. of that of the corresponding output of coal. Nevertheless, there are certain selected purposes (*e.g.* for motor-car engines and the like) for which volatile hydrocarbon oils are employed without displacing coal or gaseous fuels, and other special cases, notably steam raising in ships of war, in which liquid fuel has important advantages over coal. In respect of naval requirements, these are principally (i.) economy of space and ease in replenishing supplies; (ii.) ready and immediate response to varying loads; (iii.) possibility of forcing boiler to extreme duty in case of emergency; (iv.) absence of smoke under normal working conditions; (v.) shortness of chimney stack; (vi.) abolition of stoking; and (vii.) ability to secure and maintain higher speeds than with coal firing. Some of these advantages are also of value in relation to locomotive-boiler firing, especially in countries (United States, Russia) where petroleum is abundant. In the Report issued by the U.S. 'Liquid Fuel' Board in 1904, the relative all-round efficiencies of oil and good steaming coal, from the naval point of view, are estimated to be as 18 : 10, whilst Mr. James Holden, locomotive superintendent of the G.E.R., in giving evidence before the Royal Commission on Coal Supplies, stated that, according to his experience, petroleum fuel oil had, weight for weight, approx. twice the steam-raising power of coal in locomotive boilers. The latter estimate is probably based on the best rather than on the average results obtained with oil fuel, but certainly the ratio is not less than 3 : 2. Moreover, weight for weight, oil occupies much less space than coal, whilst oil does not deteriorate on long keeping as does coal.

Petroleum fuel oil (*see also* Petroleum). About 63 p.c. of the world's total supplies of petroleum are drawn from the United States (California, Kansas, Indian Territory, Oklahoma, Ohio, Texas, Pennsylvania, Virginia, Louisiana, and Illinois), and a further 25 p.c. from Russia (mainly the Baku oil-field); the remaining 12 p.c. is chiefly derived from Roumania, Galicia, India, and the Eastern Archipelago. The total annual output probably amounts to about 1000 million imperial gallons. Crude petroleum, in its natural state, often contains a certain amount of water in emulsified form, and also of volatile hydrocarbons. The oil should be both dehydrated and freed from volatile constituents before it can be safely transported, stored, and used as fuel. In Germany and for the British mercantile marine, the prescribed minimum flash-point for fuel oil is 150°F. (Abel test), whilst the British Admiralty require a minimum of 200°F. for warship fuel. A good fuel oil should also be sufficiently free from solid hydrocarbons to stand a temperature of 0° without solidification.

The appearance of crude fuel oil, as put on the market, varies greatly, according to its origin; some varieties have a pale colour and are mobile, others are viscous and almost black in colour. Sp.gr. varies between 0·771 and 1·06; American oil has sp.gr. 0·785–0·936; Baku oil, 0·854–0·899; Galician oil, 0·799–0·902. Whilst consisting essentially of hydrocarbons, crude oils contain small but variable percentages of N, S, and O. The nitrogen (0·25–1·0 p.c.) is present in the form of basic substances, probably of the pyridine or quinoline type; sulphur (0·5–1·5 p.c.) occurs both as alkyl sulphides (American oils) and as thiophen compounds (European oils). The following gives the ultimate composition of various crude oils:—

Origin	C	H	N	S	O	Sp.gr.
California	84·43	10·99	0·65	0·59	3·34	0·962
Texas .	84·60	10·90	—	1·63	2·87	—
,, .	85·75	12·75	—	1·47	—	—
Java .	87·1	12·0	—	—	—	0·923
Baku .	85·3	11·6	—	—	—	0·940

Of the hydrocarbon constituents, members of the following series are known to be present in petroleum: C_nH_{2n+2} *paraffin*, C_nH_{2n} *naphthenes*, and C_nH_{2n-2} . . . C_nH_{2n-12}. Mendeléjeff has concluded that all crude oils contain the same classes of hydrocarbons, but in widely different proportions. Pennsylvanian oil consists chiefly of the C_nH_{2n+2} series; Californian oil chiefly of the C_nH_{2n} (naphthene) series, together with some benzene and its homologues; Texas oil, which is dark in colour and viscous, contains principally members of the C_nH_{2n-2} and

C_nH_{2n-4} series; naphthenes C_nH_{2n}, constitute 80 p.c. of Baku oil. Of hydrocarbons, such as naphthalene, acenaphthalene, fluorene, anthracene, and phenanthrene, all of which are found in coal tar, the only one undoubtedly present in crude petroleum is naphthalene. The gross calorific value of petroleum fuel oil varies, as a rule, between 10,350 and 11,000 K.C.Us. per kilog.; the natural oils best adapted for fuel purposes are those derived from California, Texas, Mexico, and Borneo. In Russia, where a great oil-fuel industry has been developed, the residue ('astatki') after distilling off the kerosene and burning oil, is used. In applying oil to boiler and furnace work generally, the fuel must be '*atomised*' by means of a jet of high-pressure steam or compressed air in a special form of burner working on the 'injector' principle. The oil should enter the furnace as a fine spray, intimately mixed with the air requisite for its combustion. Many forms of such burners are on the market. From the chemical aspect of combustion of the oil, the use of compressed air is preferable to steam as the 'atomising' agent, although, in fact, steam is more usually employed. In other forms of burners, the 'atomising' is effected, without either air or steam, simply by forcing the oil (preheated to 130°) under considerable pressure (50 lbs. per sq. inch) through a suitable orifice.

The following typical burners may be quoted as examples: (*a*) the 'Carbogen' burner (Fig. 1), which may be used with either steam or compressed air as the atomising agent: (*b*) the 'Kermode' hot-air burner (Fig. 2), in which the oil is partially vaporised and sprayed by means of hot air at a pressure of from ½ to 4 lbs. per sq. inch. The oil enters at A, its further flow being regulated by a conical valve and slit. The air, suitably preheated, enters at the branches B and C; the portion passing through C meets the oil as it passes the oil-control valve, which is regulated by the wheel E, and both travel on together through the central tube K, in which is fixed a helix, whereby complete mixture of oil vapour and air is ensured. The two air supplies, through B and C, are separately controlled by means of the rack and pinion at M and L respectively; and (*c*) the 'Kermode' pressure-jet burner (Fig. 3), in which a supply of oil pumped into the burner through the side tube A, and passing thence through the narrow annulus D, is 'atomised' by being forced through a series of narrow grooves cut in the plug end of B, parallel to the centre line of the burner, whilst similar grooves are cut in the face of B at right angles to the axis of the burner. The grooves, as shown in H, are tangential to the cone end of the spindle C, which regulates the size of the available opening through the cap nut E. A separate forced or induced air draught is used with this burner. (*d*) A type of burner designed by Messrs. John Burden and Sons, of Bellshill near Glasgow, in which an air-injected oil spray is completely gasified and mixed with air before ignition by passage through a heated iron tube, by which means a perfectly non-luminous 'bunsen' flame of great calorific intensity is obtained.

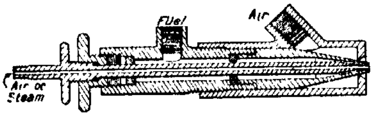


FIG. 1.

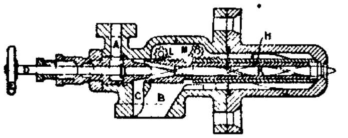


FIG. 2.

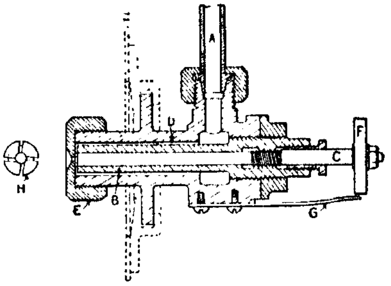


FIG. 3.

The furnace in which the 'atomised' oil is burnt should be so constructed that the flame does not come into direct contact with cold metallic surfaces. An incandescent solid surface greatly assists the completion of combustion and prevents smoke formation. (For various forms of burners, boiler-furnaces, and the like, *v.* W. H. Booth, Liquid Fuel and its Combustion, 118–221; also Redwood's Petroleum, ii. 705–714.)

Petroleum oils are also employed as fuel in internal-combustion engines. With all the earlier forms of petroleum engines, as with the modern motor-car engine, it was necessary to employ a light petroleum spirit ('petrol'), but in modern types of stationary engines, kerosene and even unrefined oils of higher boiling-points may be used. These engines usually work on the four-cycle principle. A charge of vaporised oil and air is drawn into the cylinder on the out-stroke of the piston: on the return stroke it is compressed and fired by a spark at the inner dead point. The piston is then propelled outwards by the explosion, and on the return stroke the products are expelled. Part of the heat of the products is utilised in vaporising the oil or heating the air, or both. According to trials made for the Royal Agricultural Society in 1901 by Professor Ewing, the oil consumption (American kerosene, sp.gr. 0·801, flash-point 86°F., and cal. value 10,329 K.C.Us. per kilog.) on 5 types of engines, developing 6 to 15 b.h.p., varied between 0·69 and 1·30 lb. per b.h.p.-hour. The highest thermal efficiency indicated by these trials was 20 p.c. The Diesel oil engine, which has a higher thermal efficiency than any other heat engine, burns ordinary unrefined fuel oil; the cycle consists of four strokes, namely, (1) out-stroke, in which air at atmospheric pressure is drawn into the cylinder; (2) compression stroke, in which the air is compressed to about 35–40 atmospheres, thereby becoming highly heated,– when the compression has reached about 10 atmospheres, part of the air is drawn out by a single-acting air pump and forced into a receiver (which is in direct communication with the admission valve chamber) at a pressure of about 47 atmospheres; (3) out-stroke, during the initial part of which oil, previously forced into the admission valve chamber, is sprayed into the cylinder by a small quantity of the highly compressed air in the receiver. The oil immediately burns in the hot compressed air in the cylinder, no sparking or other similar ignition device being required to start the combustion; the products of combustion then expand,—this is the working stroke; and (4) return stroke, the products are expelled from the cylinder. The makers of the engine guarantee that the consumption of crude petroleum will not be more than 0·452 lb. per b.h.p. per hour at full load, equivalent to a thermal efficiency of 35 p.c. Exhaustive trials by Mr. Ade Clark (Proc. Inst. Mech. Eng. 1903) on a two-cylinder 160 h.p. engine at Ghent, showed a thermal efficiency at full load of 32·3 p.c. per b.h.p.-hour; on a single-cylinder 80 h.p. engine, the corresponding efficiency was 31·2 p.c. The Diesel Engine Co. have produced a marine type of engine which can be coupled direct to the propeller shaft without the intervention of a clutch or other similar gear. The engine is reversible, and its speed is variable at will. Successful trials have been made with coal tar as fuel for the Diesel engine.

Literature.—Redwood, Petroleum (2 vols.), and W. H. Booth, Liquid Fuel and its Combustion.

C. Gaseous Fuels.

The great advantage of gaseous over solid or liquid fuels, for heating purposes, lies in the fact that they can be completely burned in furnaces of regenerative type with only a slight excess of air, and they are therefore specially adapted for purposes where very high temperatures on a large scale are required. The absence of smoke and ash makes their extended use, from the public point of view, eminently desirable; moreover, the possibility of gasifying coal under ammonia-recovery conditions, coupled with the much higher thermal efficiency of an internal-combustion engine as compared with a steam engine or turbine, has firmly established the position of gaseous fuels in relation to power schemes.

Natural gas. In the petroleum districts of Pennsylvania and adjoining states, natural gas issues from the strata at a depth of 500–2000 feet below the surface, and when bore holes are sunk into this accumulation, the gas rises under a mean pressure of 250–400 lbs. per sq. inch. Between the years 1821 and 1883 natural gas had been used in a limited way for illuminating and heating purposes; since 1883, however, it has undergone an extraordinarily rapid development for industrial purposes. According to the Report of the British Iron Trade Association Commission to the United States (1902), the companies engaged in the natural-gas business in the Pittsburg district were operating nearly 3000 miles of pipe lines, and the daily consumption of gas throughout the year averaged about 50 p.c. greater. Two companies brought gas from a distance of more than 100 miles. In 1914 the total production of natural gas in the U.S. was 591,866 million cub. ft., the fuel value of which was computed at 94 million dollars. The composition of the gas varies in different wells, and even in the same well after a short lapse of time; methane (64–94 p.c.) is its principal constituent; hydrogen (3–30 p.c.), together with small percentages of ethane, ethylene, carbon monoxide, and nitrogen make up the balance. The density varies between 0·45 and 0·55. Analyses of natural gas as supplied to 25 cities in the U.S. are given in U.S. Bureau of Mines Technical Paper, No. 109 (1915), according to which five of the samples contained methane only as the combustible gas, the remainder containing in addition thereto higher paraffins (particularly ethane). Processes have been installed for extracting 'gasoline' from such 'paraffinic' gases by absorption methods, using petroleum distillates or naphtha as the wash-oil. Natural gas also occurs in the southern plains of Alberta (Canada). In the Bow Island area it is obtained at 800 lbs. pressure, and, according to the Canadian Department of Mines, Memoir 93 (1917), the possible production of this field alone amounts to 50 million cub. ft. per diem; it contains $CH_4=86·7$, $C_nH_m=1·8$, $H=5·4$, $N=6·1$ p.c. Natural gas has never been found in Great Britain except in too small quantity to be industrially important; in 1895 gas was encountered during well-sinking operations at Heathfield (Sussex), at a depth of 300 feet. In 1902 gas was issuing from the bore holes at a pressure of 140–200 lbs. per sq. inch; it contained 93·16 CH_4, 2·94 C_2H_6, 1·00 CO, and 2·9 p.c. N_2, but no hydrogen.

Coal gas (coke-oven gas). Gas manufactured by the carbonisation of bituminous coals in fire-clay retorts, freed from tar, NH_3, and H_2S, and in some instances mixed with either blue or carburetted water gas, constitutes the chief public gas supply throughout the world. Within recent years the surplus gas from by-product coking plants has been purified for public use, and in localities where metallurgical coke is largely prepared, 'coke-oven gas' will probably be more extensively used in the future. The composition of coal gas varies considerably in different localities, according to the nature of the coal, the nature and disposition of the retorts, and the temperature of carbonisation. A good 'straight' coal gas as formerly supplied to the public in this country contained 45–50 H_2, 30-35 CH_4, 4·0 heavy hydrocarbons (reckoned as C_3H_6), 5·0–10·0 CO, together with not more than of about 8·0 p.c. N_2; and it had a cal. value 575 net and 645 gross B.Th.Us. per cub. ft. at 0° and 760 mm.

With the almost universal adoption of incandescent mantles for lighting purposes and the consistent increasing uses of gas for domestic heating purposes, the need of so rich a gas of high self-illuminating power diminished, a condition which opened the way for cheaper production by raising the temperature of the retort settings. In 1913, the average gross calorific value of the gas supplied in six of the largest cities of Great Britain was about 580 B.Th.Us. per cub. ft. at 60°F. and 30 in. barometer. During the war, the gas was almost universally 'debenzolised,' whereby its gross calorific value was reduced to between 450 and 500 B.Th.Us. per cub. ft. Long before the war, some gas undertakings had regularly mixed either 'blue' or 'carburetted' water-gas (*q.v.*) with the coal gas sent out of their works; and this practice is likely to grow considerably in future, especially as the Gas Regulation Act, 1920, has ordained that in future consumers shall be charged according to the Thermal units ('Therms' of 100,000 B.Th.Us.) actually supplied. It is probable that post-war gas-standards will mostly be between 400 and 500 B.Th.Us. per cub. ft.

Although the cost of manufacturing and distributing the gas militates against its use in large-scale industrial operations, where low fuel costs are of first importance, it has nevertheless made great progress in recent years (1) in the direction of supplying the needs of innumerable small-scale industrial consumers; (2) in connection with the manufacture of high-grade commodities, where the cost of the heating operation is of less consequence than the certainty of attaining a particular result within a given time (*e.g.* in the heat treatment of special steels or alloys); and (3) for brass and aluminium melting, pipe welding, glass annealing, the tempering and forging of tools, &c. Thus, for example, 13 of the principal firms in Sheffield used, in 1917, upwards of 1200 million cub. ft. of coal gas for industrial operations.

Tests carried out at the Imperial College of Science and Technology, London, have shown that a well-constituted modern gas fire, in which the columnar fire-clay 'radiant' material is properly disposed in relation to the atmospheric burners, will not only completely burn the gas without a vestige of carbon monoxide escaping into the room, but it has an unexpectedly high 'radiation' efficiency. The total '*radiation*' from such a fire will vary from 45 to 50 p.c., whilst about 30 p.c. of the *net* heat generated passes directly into the flue, the balance being 'convected' into the room. Also H. James Yates has designed a 'ventilating gas fire' which combines the aforesaid high 'radiant' efficiency with a ventilating capacity nearly equal to that of an open coal fire.

Large surpluses of 'coke-oven gas,' which is little, if at all, inferior to many town gas supplies, are now available for steam raising or as gas-engine fuel. The efficiency of the gas when burnt in Lancashire boilers rarely exceeds 65–70 p.c., and with coal at 10s. per ton the cost of the gas for steam raising does not exceed 3*d*. per 1000 cub. ft. With the rapid extension of by-product coking plants in Great Britain, the proper utilisation of the energy represented by the surplus gas has become a problem of national importance. An average 'debenzolised coke-oven gas' will contain $CO_2=2·0$, $CO=6·0$, $C_nH_m=2·0$, $CH_4=25·0$, $H=55·0$, $N=10·0$ p.c. In 1910 Parliamentary sanction was obtained for supplying gas from the Brackley Coke Works to the Urban District of Little Hulton (Lancs.), and the Corporation of Middlesbrough now draws its entire public supply of gas from regenerative by-product ovens at a neighbouring ironworks.

Producer gas. For the cheap and rapid production of gaseous fuel for industrial purposes, there is no better process than the gasification of solid fuels (peat, bituminous coal, coke, or anthracite) by means of a mixed air-steam blast (sometimes air alone is employed) in some form of gas 'producer,' whereby the fuel is converted into gas containing some 35–45 p.c. of combustible constituents (CO, H, and CH_4). A modern gas producer consists of a cylindrical furnace, 6–12 feet internal diameter and 10–15 feet high, lined with fire-brick with an outer mild steel casing, and usually water-sealed at the bottom. Means are provided (1) for the introduction of the blast through some form of grate or twyer fixed immediately above the level of the water in the seal, and its regular distribution through the bed of incandescent fuel (usually 3–5 feet in thickness) which rests upon a lower bed of ashes; and (2) for the charging in of the raw fuel through (usually) some form of bell hopper fixed centrally on the top of the producer, round which are arranged a number of equidistant poking holes closed by iron balls. The gas outlet is fixed near the top of the cylindrical furnace. Taking as a typical example a producer working with a mixed air-steam blast on a common bituminous coal, the chemistry of gasification may be epitomised as follows. When a fresh charge of fuel is dropped into the furnace, it first of all undergoes a process of distillation on the top of the fire, whereby H, CH_4, tarry hydrocarbons, CO, together with small quantities of NH_3, H_2S, &c., are evolved, probably in much the same proportions as in the ordinary retort distillation of coal; olefines and higher paraffins are, however, so rapidly decomposed that they do not, as a rule, appear in the gas passing out of the producer. The carbonaceous residue (coke) is subsequently completely gasified in the lower layers of the incandescent fuel bed, by interaction with the ascending air-steam blast, yielding a mixture of CO_2, CO, H, and N, together with further small proportion of NH_3 and CH_4. The proportion of CO_2, CO, and H leaving the incandescent coke bed depend upon the steam saturation temperature of the blast, which also largely determines the temperature gradient throughout the fire. In order to fully understand the chemistry of the process, it is necessary to separately consider the interaction between incandescent carbon and air and steam respectively. In a solid bottom producer operated with a *dry*-air blast, the initial action of the oxygen upon the incandescent carbon is rapidly succeeded by the reversible reaction $2CO \rightleftharpoons C+CO_2$ in which the state of equilibrium is a function of both temperature and the partial pressures of the CO and CO_2. It can be demonstrated that the time required for the establishment of this equilibrium, at the temperatures which prevail in the fuel bed, is far shorter than that occupied by the gaseous mixture in traversing the fuel. According to Rhead and Wheeler's experiments (Chem. Soc. Trans. 1910, 2178), the equilibrium in the system $2CO \rightleftharpoons C+CO_2$ at atmospheric pressure varies with temperature as follows :—

Temp.	Per cent. CO_2	Per cent. CO
850°	6·23	93·77
950°	1·32	98·68
1050°	0·37	99·63
1200°	0·06	99·94

results which are in agreement with the thermodynamical equation

$$\frac{19{,}500}{T_{abs.}} + \log_e \frac{C^2_{CO}}{C_{CO_2}} = 20{\cdot}4.$$

As the change from 2CO to CO_2 involves a diminution in volume, it can be predicted on thermodynamical grounds that a lowering of the partial pressures of the CO_2 and CO, consequent on dilution with N in the producer gases, will affect the equilibrium in the same direction as an increase in temperature, *i.e.* it will tend to increase the ratio CO/CO_2 at any given temperature. The temperatures in the active zones of the fuel bed of an air-blown producer gasifying coal or coke may vary between 1250° and upwards of 1400°, and with good coke it is easily possible to generate a gas containing 0·5 CO_2, 33·0 CO, 1·5 H, and 65·0 p.c. N. But since the combustion of carbon to CO liberates approximately 30 p.c. of its total heat of combustion, not only would the thermal efficiency of the gasification in an air-blown producer, reckoned on the cold gas, be low, but the high temperatures in the fuel bed would cause serious clinkering troubles in cases where the fuel leaves a fusible ash. In the Thwaite cupola producer (30 feet high and 6 feet internal diameter), where a dry-air blast, forced in through a series of twyers near the bottom, is employed, it is usual to add a certain proportion of limestone to the fuel charge in order to form a liquid slag with the ashes, which is tapped at intervals through a slag-notch. Working on a Lancashire slack coal, this producer yields a gas containing 2·0 CO_2, 29·0 CO, 5·35 H, 2·05 CH_4, 61·6 N, of cal. value 130·8 *net*, and 138·7 *gross*, B.Th.Us. per cub. ft. at 0° and 760 mm.

Steam reacts with carbon in two ways, namely, (1) $C+2H_2O=CO_2+2H_2$, and

(2) $C+H_2O=CO+H_2$,

and both reactions are strongly endothermic. At 500°–600° (1) predominates; as the temperature rises (2) gradually asserts itself, until at 1000° and upwards it occurs exclusively. The function of the steam in a gas producer is, therefore, to absorb some of the heat liberated during the partial 'air combustion' of the carbon to CO by doing chemical work, thereby raising the potential energy of the resulting gas at the expense of some of its sensible heat. Incidentally, also, clinkering troubles with a fusible ash are greatly diminished by the admixture of steam in the blast. Where a large proportion of steam is used, the composition of the resulting gas is appreciably affected by the reversible system $CO+H_2O \rightleftharpoons CO_2+H_2$, of which the equilibrium constant, $\frac{CO \times H_2O}{CO_2 \times H_2}=K$, increases with temperature (according to O. Hahn, K=0·81 at 786°, 1·54 at 986°, and 2·10 at 1205°). The operation of this reversible reaction must also be considered when a producer gas passes through the hot regenerators of an open-hearth furnace.

The influence of varying blast-steam saturation temperatures upon the composition and yield of the gas from a Lancashire bituminous coal containing C=78·0, H=5·4, S=1·0, N=1·4, O=10·0, ash=4·2 p.c., and yielding 36 p.c. 'volatiles' at 900°, is shown in the tabulated results below of a series of gas-producer

Average depth of incandescent fuel	3 feet 6 inches					7 feet				
Average rate of gasification (day-shift) per hour per producer	22·5 cwts.					11·5 cwts.				
Steam saturation temperature of blast	45°	50°	55°	60°	70°	60°	65°	70°	75°	80°
Percentage composition of the gas: Carbon dioxide	2·35	2·50	4·40	5·10	9·25	5·25	6·95	9·15	11·65	13·25
Carbon monoxide	31·60	30·60	28 10	27·30	20·85	27·30	25·40	21·70	18·35	16·05
Hydrogen	11·60	12·35	15·45	15·50	19·75	16·60	18·30	19·65	21·80	22·65
Methane	3·05	3·00	3·00	3·05	3·45	3·35	3·40	3·40	3·35	3·50
Nitrogen	51·40	51·55	49·05	49·05	46·70	47·50	45·90	46·10	44·85	44·55
Total combustibles	46·2	45·05	46 60	45·85	44·05	47·25	47·10	44·75	48·50	42·20
Calorific value of the gas, B.Th.U. per cubic foot at 0° and 760 mm. Gross	180·0	178·5	180·8	178·7	175·5	185·6	185·4	177·5	172·0	169·5
Net	170·5	168·7	169·1	166·9	161·0	173·0	172·0	163·3	157·3	154·3
Yield of gas, cubic feet, at 0° and 760 mm. per ton coal	133,700	132,500	132,700	135,000	—	138,250	134,400	141,450	145,800	147,500
Steam added to blast, lbs. per lb. coal	0·2	0·21	0·32	0·45	—	0·45	0·55	0·80	1·10	1·55
Percentage steam decomposed	all	all	all	76·0	—	87·0	80·0	61·0	52·0	40·0

trials (each extending over a continuous period of 100–130 hours) carried out by Bone and Wheeler in 1906–7 (Jour. Iron and Steel. Inst. 1907, i. 126; 1908, ii. 206).

In these trials it was also proved (1) that on gasifying an ordinary bituminous coal by means of a mixed air-steam blast, about 92·5 p.c. of the carbon in the fuel is converted into permanent gas (CO_2, CO, and CH_4), another 6·3 p.c. appears as tar, and the remaining 1·2 p.c. is lost in the ashes. These proportions are independent of the blast-steam saturation temperature. (2) That with blast-steam saturation temperatures up to and including 55°, the whole of the steam in the blast is decomposed in passing through the fuel bed; as the saturation temperature is raised above this limit, the proportion of the steam decomposed progressively diminishes, although the absolute quantity (per lb. of fuel) increases. (3) That increasing the effective depth of fuel bed beyond 3 feet 6 inches has no influence upon either the composition of the gas or the practicable rate of gasification. (4) That the thermal efficiency of the gasification reaches a maximum at blast-steam saturation temperatures between 50° and 60°, and that the best quality of gas for furnace purposes is produced with a saturation temperature of 50°.

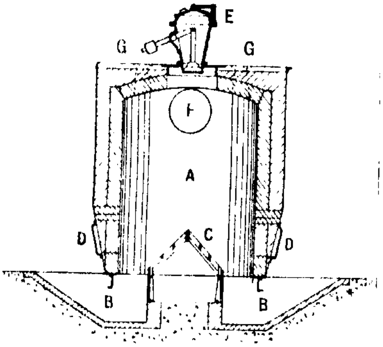
In gas generated for furnace purposes it is important that the CO content should be as high as possible, and that the H content should not exceed about 12–14 p.c.; moreover, for a regenerative furnace supply the gas leaving the producer should be in a hygroscopic condition such that the proportions of CO_2, CO, H, and H_2O shall substantially conform to the equilibrium *ratio* corresponding to the highest temperature of the regenerator (say 1200°), namely, $\frac{CO \times OH_2}{CO_2 \times H_2} = 2\cdot0$. This latter requirement is fulfilled by a gas containing 2·5 CO_2, 30·6 CO, 12·35 H (such as may be generated with blast-steam saturation temperature of 50°), and leaving the producer in a hygroscopic condition corresponding to saturation at 20°. Such a gas will leave the producer heavily charged with tarry vapours, and at a temperature of 500°–600°; it usually passes on to the furnace through large fire-brick lined mains, without being cleaned or cooled, accumulations of tar, soot, &c., in the mains being burnt out in a current of air at the end of each week's run (*vide* also W. A. Bone, Producer Gas, with special reference to Steel Works Requirements, Journ. W. of Scotland Iron and Steel Institute, 1911).

In gas generated for power purposes, the actual composition is not so important, provided that the total content of combustible constituents is high, and in such cases the gas may be generated under conditions permitting of the recovery of a large proportion of the N in the fuel as NH_3. A gas supply for internal-combustion engines must be both thoroughly cleaned and cooled down to atmospheric temperature before delivery to the engine.

The main points to be considered in relation to gas-producer design are: (1) the easy and accurate control of the blast-steam saturation temperature; (2) a suitable form of grate or twyer which should permit of a rapid rate of gasification, together with uniform distribution of the blast, through the fuel bed; (3) the contour of the furnace body; and (4) the arrangements for charging the producer and removal of the ashes. One of the earliest forms of gas producers (Ebelmen, 1840) was of the cupola type, in which charcoal or coke was gasified, with a positive blast introduced through twyers, limestone being added to the charge (if necessary) to flux the ash. In 1845 Ekman, a Swedish ironmaster, designed a furnace and producer combined, for which the fuel was charcoal. The producer itself consisted of a cylindrical fire-brick chamber, enclosed in an iron casing, a space being left between the brickwork and the casing through which the air supply was admitted and preheated on its way to the fire. In 1861 the Brothers Siemens patented their well-known producer for use in connection with their new regenerative furnace. This producer consisted of a fire-brick chamber, rectangular in section, the front of which was inclined at an angle of 45°–60°, provided with a grate at the bottom, through which a current of air was induced. Below the grate was a trough of water, which, on evaporation, by heat radiated from the grate, added a certain proportion of steam to the induced air supply. Subsequently the front of the producer was closed by an iron door, and the air supply forced in under the grate by steam injection. This producer was the first to successfully gasify a bituminous coal; it was capable of generating a fairly good quality of gas, but its rate of gasification was low. In 1876 Messrs. Brooke and Wilson patented a producer consisting of a cylindrical chamber having a solid hearth, but no fine bars. The mixed air-steam blast was obtained by steam injection, and was introduced into the fuel bed by means of a box-shaped casting which traversed the middle of the hearth. In 1882 Mr. Wilson patented a form of generator on which ash and clinker were automatically removed by means of two worm screws revolving in a water seal. Water-sealed producers have now almost entirely superseded the older solid or bar-bottom types.

The Duff producer (Fig. 4) may be cited as a modern producer of simple design; it consists of a cylindrical chamber, A, 7–10 feet internal diameter, with a 9-inch fire-brick lining within an outer steel shell. At the bottom of the lining is a circular angle-iron casting, which dips into the water seal in the trough BB. The 'Duff' grate, or blast grid, C, is a ╱╲-shaped structure, with transverse grids extending as a ridge across the producer immediately above the water seal; the air-steam blast enters the space beneath the grate, and the grid ensures its uniform distribution over a considerable area of the fuel bed. The latter (which, as a rule, extends to a height of about 3 feet above the apex of the grate) is supported upon a bed of ashes, which extends downwards from the grate level into the water trough. In the lower part of the shell of the producer, and on a level with the grate, are inserted cleaning doors DD. The fuel is charged intermittently into the furnace through the belled hopper E, and the gas outlet is at F; the dotted lines at GG indicate poking holes. Ashes are withdrawn from the water trough at regular intervals in quantity corresponding to the rate of accumulation in the furnace. A producer of 10 feet internal diameter will gasify 10 cwts. of coal per hour, or about 15 lbs. per sq. ft. of fire area.

In Fig. 5 is shown the latest form of the Mond producer, which, although designed with special reference to ammonia-recovery practice, is eminently adapted to all working conditions. The chief features about this producer are (1) the annulus A between the inner fire-brick lining and outer steel shell through which the incoming preheated air-steam blast passes before reaching the grate; (2) the hanging bar grate B, which takes the shape of an inverted truncated cone, with spaces between the bars for the admission of the blast, an arrangement which ensures an adequate grate area and a very uniform and effective distribution of the blast in the fuel bed; and (3) the large bell C at the top of the producer below the charging hopper D, which is supposed to expedite the preliminary distillation of the raw fuel. The Mond producer is usually worked with a very deep fuel bed, as indicated in the diagram, but if the bell C be dispensed with, a much shallower fuel bed may be used with advantage. In Fig. 6 is shown the B.W. producer, which, with an improved form of hanging bar grate, is specially adapted for rapid gasification with a shallow fuel bed. In a producer of this type, 10 feet internal diameter, from 20 to 25 cwts. of coal (equal to 30–35 lbs. per sq. ft. of fire area) may be gasified per hour.



SECTION THROUGH WATER SEAL.

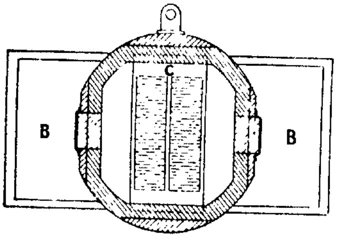


FIG. 4.

Some years ago attention was drawn to the automatic and continuous feeding of the fuel into producers so as to ensure a more even distribution over the fire bed, and more uniform working conditions. The 'George' feed of the Morgan producer (Fig. 7) satisfactorily effected this purpose. The essential feature of this device is an inclined and slowly rotating water-cooled feeding spout A, fixed immediately under the charging hopper B, the fuel being

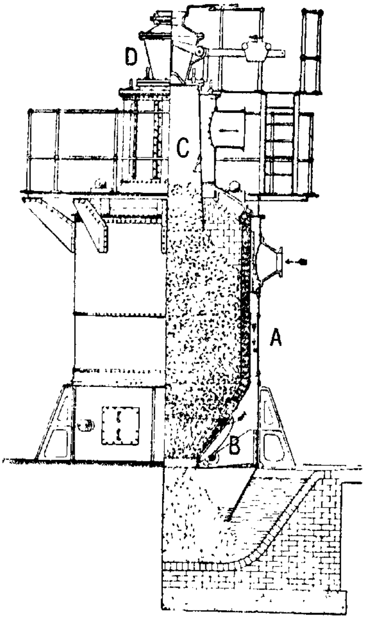


FIG. 5.

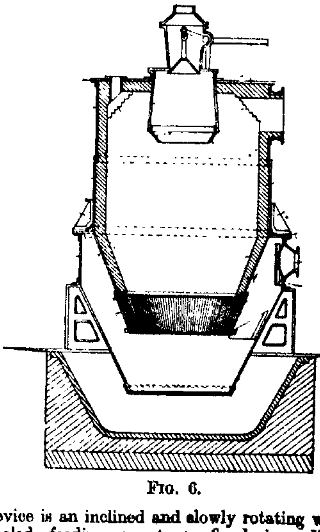


FIG. 6.

continuously forced from B into A by the slowly revolving circular disc, C, working up against the fixed bracket D. The producer itself is water sealed, and circular in section, but tapering from the middle downwards. The blast is introduced through the central dome E, and the gas outlet is at F. The producer may be worked with a shallow fuel bed (3 feet thick), and with a fire of 10 feet diameter will gasify about 10 cwts. of fuel per hour.

The Kerperley producer (Fig. 8) embodies the latest device for the automatic and continuous removal of ashes, consisting of a revolving conical grate, A, fixed eccentrically upon the foundation, and provided with a flattened top. The cone comprises a number of plates through which the steam-air blast reaches the fire. The grate is fixed in one piece with the shallow iron water trough BB, which is continuously rotated at the slow rate of one revolution every 2½–3 hours. The lower part of the producer surrounding the zone of active chemical action is water-jacketed CC, in order that no incipient clinkers can adhere to the cold side plate. The slowly revolving eccentric grate disintegrates clinkers before they attain large dimensions, and, pushing the ashes outwards into the water trough, causes them to be automatically discharged by their coming up against a fixed scraper. The Morgan producer also is now fitted with a mechanical revolving grate (Fig. 9), which, besides effecting automatic discharge of ashes, considerably increases the gasifying capacity of the producer.

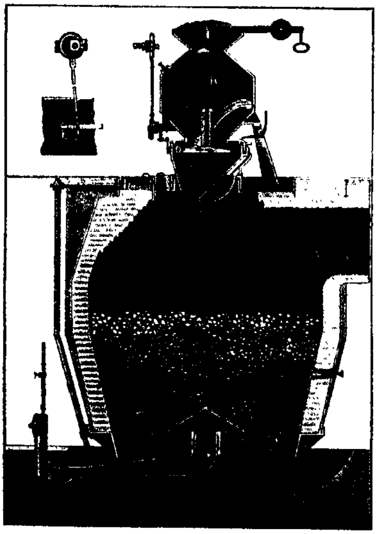


FIG. 7.

A still more recent mechanical development in gas-producer practice is the employment of water-cooled rotatory poking devices of which the Chapman Floating Agitator is a typical example. This appliance combines an automatic feed with a slowly rotating water-cooled stirring arrangement which keeps the upper layers of the fuel bed constantly agitated, whereby 'caking' is prevented; it may be fitted on to existing types of producers, no matter whether they have static or rotating grates. In the latest form of Morgan 'Gas Machine,' the coal is automatically fed into the producer, whilst continuous removal of ash is effected by making the body of the producer to rotate slowly and automatically sweeping the entire bottom of the water-sealed ash-pan by a suitable spiral-shaped bar or plough. All need of poking is eliminated by using an adjustable water-cooled 'leveller,' which 'floats' on the slowly rotated fuel-bed and keeps it constantly levelled.

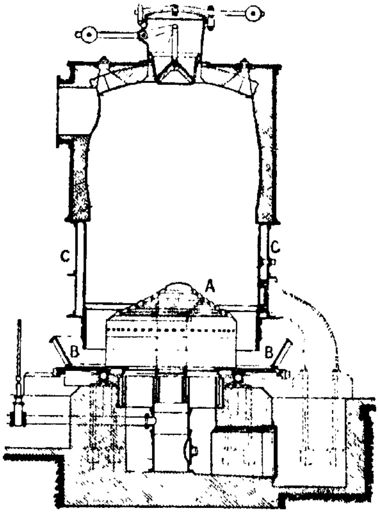


FIG. 8.

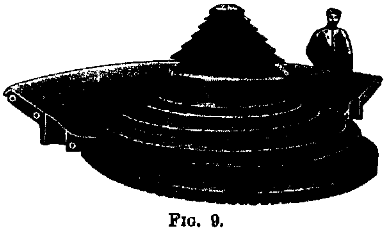


FIG. 9.

All large gas producers are blown on the pressure system either by means of steam injection or preferably by a suitable fan or blower, steam or electrically driven. The pressure required is only 3–6 inches water gauge, according to the thickness of the fire. In the case of a blower-produced blast, the requisite steam is introduced through a lateral opening into the air duct a few feet before it enters the producer; perfect control and adjustment of the blast-steam saturation temperature is of great importance in relation to uniform working.

For the cleaning and cooling of producer gas for gas engines, various arrangements of plant are employed, comprising (1) a dust-catching chamber; (2) atmospheric condenser, usually of annular type; (3) water-sprayed coke or 'hurdle' scrubbers; (4) water-sprayed fans; and, finally (5) sawdust scrubbers or other equivalent devices for removal of tar fog.

For small (up to 200 h.p.) power installations, producers in which the blast is induced by the suction of the engine cylinder ('suction producers') are now largely employed with anthracite or coke as fuel. The first successful attempt to operate a producer by suction in conjunction with a gas engine was made by Léon Bénier, in 1896, who employed a suction pump, placed side by side with the engine cylinder and driven by means of a connection with the fly-wheel axle. Soon afterwards the suction of the engine itself, on the out-stroke of the piston, was substituted for the Bénier suction pump, thus cheapening construction, and at the same time reducing fractional losses. By 1901 'suction' power plants were established on the market, and their use has since steadily extended. Such a plant (as illustrated in Fig. 10) consists of the following essential parts: (1) A fire-brick-lined *generator*, A, of cylindrical section, in which the fuel is gasified by means of an air-steam induced draught; the fuel is introduced through an *air-tight feeding hopper*, B, which drops it into a *storage and distillation bell*, C, situated within the generator. The fire rests upon a horizontal grate under which is a shallow chamber, D, with a solid bottom, and a lateral opening communicating with the air and steam supplies. (2) A *vaporiser*, E, which may be either within or without the upper part of the shell of the generator, in which a regulated water supply is vaporised, usually at the expense of some of the sensible heat of the hot gas leaving the generator, or sometimes by the heat of the fire. (3) A water-sprayed *coke scrubber*, F, for cooling and washing the gas; and (4) an *expansion box*, G, which serves the double purpose of a gas reservoir for the engine, and, on the suction stroke, of minimising the jerkiness of the suck. The generator is started up by kindling a wood fire on the grate with a layer of coke or anthracite above. The fire is blown up by means of a hand fan, which is a necessary auxiliary to the apparatus. During the starting-up period, the products of combustion are sent into the atmosphere through a vent pipe, but as soon as a rich enough gas is generated (about 20–30 minutes from the start), the engine is started and the fan shut off. A typical 'suction gas,' generated from gas coke with air saturated with steam at 51·7°, contains $CO_2=5{\cdot}10$, $CO=25{\cdot}45$, $H=13{\cdot}10$, $CH_4=0{\cdot}28$, and $N=55{\cdot}32$ p.c., its *net* calorific value being 127 B.Th.Us. per cub. ft. at 0° and 760 mm. The thermal efficiency of the gasification, allowing for the power required to draw the gases through the system, and based on the net calorific values of coke and gas respectively, is about 78·5 p.c. The fuel consumption on a suction plant is about 1 lb. or even slightly less, per b.h.p. developed, the water consumption for scrubbing the gas being about 1·2 gallons per b.h.p.

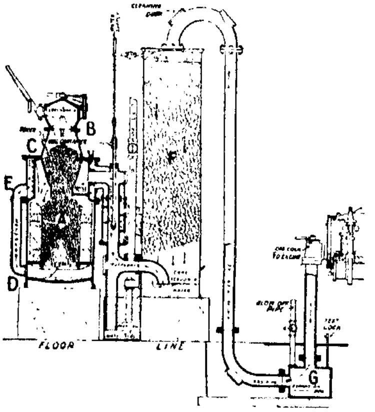


FIG. 10.

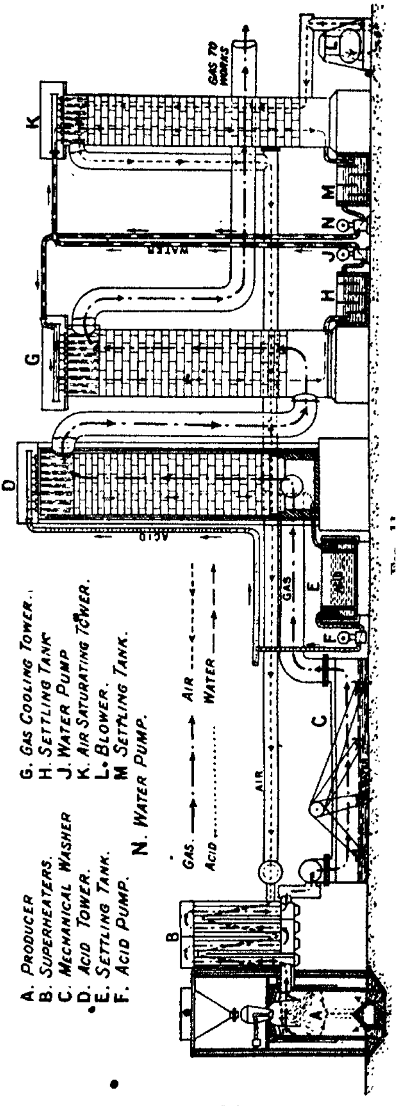
Ammonia-recovery systems. The solution of the problem of the gasification of coal under conditions which permit of the recovery of a large proportion of its nitrogen as ammonia, was due to the late Dr. Ludwig Mond. The best practical results are obtained by working the producer with a blast-steam saturation temperature of 85°, the mixture of air and steam being preheated to about 250° before it enters the fuel bed. There is carried into the producer by the blast about 2 lbs. of steam for every 1 lb. of coal gasified; one-third only of this steam is decomposed, by interaction with carbon, in passing through the fuel bed, the remaining two-thirds passing with the hot gases out of the producer. The outstanding features of the process are (1) that, owing to the cooling influence of the large proportion of steam in the blast upon the fuel bed, the low temperature interaction $C+2H_2O=CO_2+H_2$ predominates over the high temperature 'water-gas' reaction, $C+H_2O=CO+H_2$, so that the resulting gas (*e.g.* 17·0 CO_2, 11·0 CO, 24·0 H, 3·0 CH_4, and 45·0 N) has a high hydrogen and low carbon monoxide content as compared with ordinary producer gas; and (2) that for economical working it is necessary that the large proportion of steam leaving the producer shall be conserved to the system by some efficient recuperative arrangement. From a coal containing between 1·2 and 1·6 p.c. N it is possible to obtain up to 90 lbs. per ton of ammonium sulphate, together with about 150,000 cub. ft. of gas (at 0° and 760 mm.) of calorific value about 150 gross and 135 net, B.Th.Us. per cub. ft. at 0° and 760 mm. According to the Mond system of ammonia recovery and steam recuperation, as originally designed, the gas leaves the producer heavily charged with steam and tarry vapours at a temperature of 500°–600°. It then traverses the central tubes of a series of three annular 'superheaters,' indicated by B in the diagram (Fig. 11), each about 20 feet long. The incoming steam-air blast passes through the annulus between the central and outer tubes in the reverse direction. The temperature of the gas is thus reduced to about 300°, whilst that of the blast is raised to about 250° (further 'superheating' of the blast occurs as it subsequently

traverses the annulus between the fire-brick lining and the outer steel casing of the producer itself). The partly cooled gas next passes through a long rectangular and water-sealed chamber (the 'mechanical washer'), C, where it encounters a water spray thrown up by a series of revolving dashers, by which means dust, soot, and a large amount of heavy tar are removed, and the gas itself further cooled to about 100°. It next passes up the lead-lined scrubbing tower D, packed with perforated bricks or tiles, down which an acid liquor containing 36–38 p.c. of ammonium sulphate *plus* 2·5 p.c. of sulphuric acid is sprayed, the volume of liquor being so adjusted in relation to the upward flow of gas that the latter leaves the tower at a temperature of 80° and free from ammonia. The tarry liquor from the tower is passed into an open tank provided with suitable partitions, in order to eliminate any small quantity of surface tar in it. To the main bulk of the clear liquor is added a regulated quantity of sulphuric acid, after which it is again pumped up to the top of the acid tower D. A portion of the clear liquor is, however, removed from the circuit, and, after treatment with heavy oils (if necessary) to remove tar, is evaporated to crystallising-point in a special lead-lined vacuum evaporator furnished with steam coils. After separation of ammonium sulphate, the mother liquor is pumped back into the main-liquor circuit. The ammonia and tar-free gas, on leaving the acid tower at 80°, is passed up the 'gas cooling tower' G, where it encounters a downward spray of cold water, so regulated that whilst the gas is cooled down to about 60°, and rendered substantially free from tar, the water is heated up to 75°–78°. The gas passes onwards to the place of consumption through a second water-sprayed cooling tower in which it is further cooled to 30°, at which temperature it contains only 4 p.c. by volume of water vapour. But if it is intended for gas engines it should be further cooled down to within a few degrees of the atmospheric temperature, and be also passed through a sawdust scrubber to remove the last traces of tar.

The hot water from the 'gas-cooling tower' is passed through a tar separator, after which it is pumped up to the top of the 'air-saturating tower' K down which it is sprayed. The air blast for the producer is forced up this tower by means of a blower; in this way the blast is heated up to and saturated with steam at 75° at the expense of the hot water. A further quantity of live steam is added to the air blast as it passes forward to the superheaters in order to raise its steam-saturation temperature to 85°.

The chief drawback to the original Mond system was the large capital outlay involved, which rendered ammonia recovery unprofitable unless the coal gasified exceeded 180–200 tons per week. Moreover, the gas, being rich in hydrogen and poor in carbon monoxide, is not well suited for open-hearth steel or glass-melting regenerative furnaces.

Successful efforts have been made to simplify the mode of ammonia recovery by the substitution of rectangular horizontal washers, constructed of steel or iron work and rendered resistant to the acid liquor by special treatment, for the expensive lead-lined vertical acid tower, and by making the sulphate liquor play the double *rôle* of an absorbent for the ammonia in the gas and an agent for the transfer of undecomposed steam back to the producer blast. As an example of this type of plant, the Crossley and Rigby system may be described with reference to Fig. 12. The generator A is central blown with a special rotary conical grate (1 revolution in 4 hours), which gives an even distribution of blast



through the deep fuel bed and minimises clinker formation. The blast enters the fuel bed preheated to 280° and with a steam-saturation temperature of 85°. The gas, on leaving the producer, passes through the tubular 'superheater' B, so designed as to give a maximum of heating surface combined with facility of cleaning. The latter operation may be effected whilst the plant is running by means of a corkscrew cleaner inserted through holes provided at the top. The function of the superheater is to effect a transfer of part of the sensible heat of the outgoing hot gas to the incoming steam-air blast. The partly cooled gas next passes onwards to the 'washer condenser' C, consisting of five compartments, in the first two of which it meets with a water spray whereby it is freed from dust and heavy tarry vapours; the steam generated is subsequently recovered. In the remaining three compartments the gas is washed with a spray of sulphate liquor containing 0·5 p.c. of free acid, which is circulated by gravity flow in a direction contrary to that of the gas. The absorption of ammonia is complete, whilst at the same time the gas is satisfactorily cooled and most of the undecomposed steam leaving the producer is condensed. After leaving the washer condenser, the gas is slowly filtered through the dry coke scrubber D whereby all trace of sulphate liquor spray is removed. The hot liquor from the washer condenser passes by gravity flow into the well E whence it is pumped into the air-saturating chamber F where it flows and is sprayed by paddles in a counter direction to the cold-air blast created by the blower G. The liquor is thereby cooled and flows by gravity back to the washer condenser C, whilst the air blast is warmed and leaves the chamber (*viâ* the coke scrubber H) saturated with steam at 75°. A constant proportion of sulphate liquor is withdrawn from circulation and delivered into the closed evaporator K, where it is concentrated to crystallising-point. A portion of the concentrate is run off at frequent intervals into the crystallising trough L, where, after cooling and draining, the sulphate is dried and the mother liquor returned by gravity flow to the washer condenser C. The steam from the evaporator is conveyed by an overhead pipe to the base of the coke scrubber H, where it enters the air blast already saturated with steam at 75°. The steam-air blast then passes forward, *viâ* the coke scrubber H and the superheater B, to the producer. Owing to a special treatment of the iron and steel used in the construction of the plant, all leadwork is eliminated, except in the acid storage tank and the sulphate concentrating and crystallising apparatus. In consequence of the greatly reduced capital cost, as compared with the original Mond system, it is now possible to carry out ammonia recovery when gasifying only 100 tons per week. From a producer coal of average quality, containing 1·20–1·25 p.c. N, and up to 10 p.c. ash, it is possible to recover 90–100 lbs. of sulphate per ton, together with 140,000 cub. ft. of gas (at N.T.P.) containing 16·5–17·0 CO_2, 10·5–11·0 CO, 26·5–27·0 H_2, and 2·6–2·8 CH_4.

Among the most recent developments in regard to ammonia-recovery practice may be mentioned (1) an interesting attempt to economise steam by gasifying the fuel in a water-

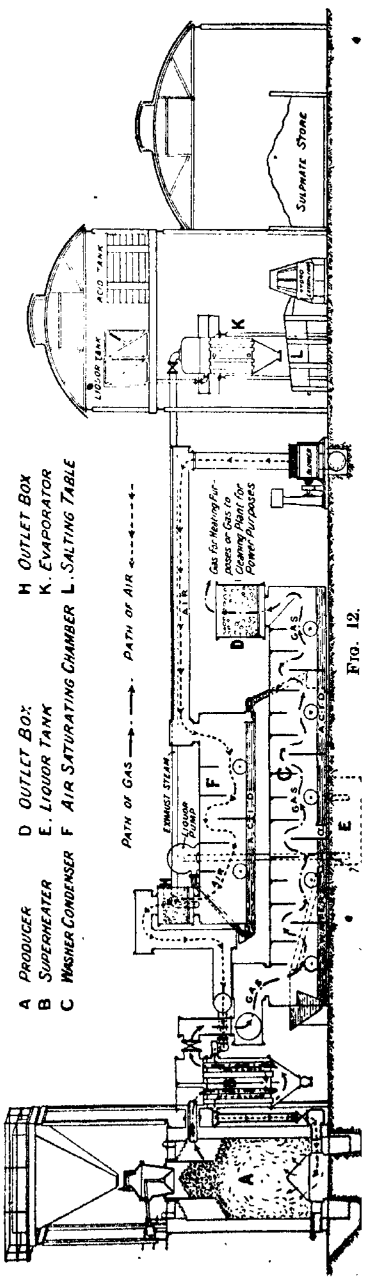


Fig. 12.

jacketed generator, as embodied in the Moore system, whereby it is claimed that the steam required to produce from 80 to 90 lbs. of ammonium sulphate from a ton of coal need not exceed the weight of fuel gasified, the resulting gas containing CO_2=10·0, CO=20·0, H=20·0, CH_4=3·0, and N=47·0 p.c. (*vide* Iron and Coal Trades Review, February 21, 1913); and (2) the Lymn system, in which the plant has been entirely re-modelled with a view to reducing its capital cost (*vide* the writer's book on Coal and its Scientific Uses, pp. 366–370).

Blast-furnace gas Within recent years the problem of better utilising the waste gases from iron blast-furnaces as a source of power has assumed great industrial importance. A furnace smelting an average grade of ore, with coke as fuel, will yield per ton of iron produced about 185,700 cub. feet of gas at 15° and 760 mm. containing approximately 10·0 CO_2, 30·0 CO (this may include from 0·5 to 1·0 H) and 58·0 N, of calorific value approximately 95–100 B.Th.Us. per cub. ft. For a furnace with an output of 1000 tons of pig iron per week, the production of gas will average 1·114 million cub. ft. per hour, the potential energy of which is rather more than half that of the coke charged into the furnace. Until the year 1837, when the French ironmaster Dufaur drew attention to the matter, this immense amount of energy was entirely wasted. The classical investigations of Bunsen at Verkerhagen in 1838, and of Bunsen and Playfair at Alfreton in Derbyshire in 1844–5 (Brit Assoc. Reports, 1845; reprinted, 1903, by the Iron and Steel Inst.), finally led to the utilisation of the gases for (1) heating the blast for the furnace, and (2) boiler firing. Special 'hot-blast' stoves, on the regenerative principle, were designed to effect the first purpose by E. A. Cowper and by Thomas Whitwell in 1865, whilst for steam raising the gas was burnt in a fire-brick-lined combustion chamber attached to a Lancashire boiler. In this way about 40 p.c. of the gas was utilised for heating the blast, another 10 p.c. would be lost at the bell, leaving 50 p.c. to be used to raise steam for driving the blowing engines, the furnace hoists, and other mechanical appliances in connection with the plant. But the combined efficiency of boiler *plus* steam engine was always very low; thus in 1902 it was estimated by a Cleveland engineer that with the best type of water-tube boiler only about 54 p.c. of the heat developed by the combustion of the gas is actually transmitted to the water, and that the combined efficiency of boiler and blowing engine was somewhat less than 7 p.c. All this has been changed by the rapid development of the large gas engine during 1895–1905, which has increased the efficiency of power production from blast furnace gas something between three- and fourfold as compared with the old steam plants. Gas engines developing up to 2000 b.h.p. per unit have now been installed in most of the German and many British and American ironworks, realising in actual practice a thermal efficiency of conversion 'gas—b.h.p.' of 25 p.c., and of 'gas—e.h.p.' of 20–22 p.c. As an illustration of what this improved practice implies, the following figures may be quoted for a plant of five furnaces smelting 5000 tons of iron per week from calcined Cleveland ironstone; the hourly production of gas is 5,500,000 cub. ft., of which not more than 1,100,000 would be required for generating the blast in a gas-driven blowing engine, another 1,650,000 for heating the blast, leaving a surplus of about 2,750,000 cub. ft. for employment in the steel works (heat and power).

Indeed the time has now arrived when, with a proper concentration and arrangement of the various producing units (by-product coke ovens, blast furnaces, gas-power house, steel furnaces, soaking pits, and electrically-driven rolling mills), and utilising to the best advantage all the surplus coke-oven and blast-furnace gases, ironstone may be brought in at one end of the plant and finished steel sections turned out at the other, with no more expenditure of fuel than the amount of coal that is required to make sufficient coke to smelt the ironstone in the blast furnace (*vide* T. C. Hutchinson, Jour. Iron and Steel Inst. 1913, ii. 110; and W. A. Bone's 'Coal and its Scientific Uses,' pp. 409–421).

The gas, as it leaves the furnace at a temperature of 300° or thereabouts, is heavily charged with dust, which must be reduced by washing to infinitesimal proportions before it is fit for delivery to the engines. The cleaning of the gas is usually accomplished in two or three stages, namely: (1) 'dry cleaning' (by means of any ordinary type of dust catcher), which may reduce the dust down to between 2 and 8 grams per cub. metre; (2) preliminary water washing (*e.g.* in the Bian washer, consisting of a cylindrical steel chamber along the axis of which there slowly revolves a horizontal shaft carrying a series of circular discs of thick wirework with a coarse mesh, the lower half of which is submerged in water; the dusty gas is partly cleaned by passing through the films of water between the wire meshes); this may reduce the dust down to 0·5 gram per cub. metre; and (3) a final cleaning in some form of centrifugal apparatus in which the gas is violently churned up with a fine spray or stream of water (*e.g.* the Theisen washer). Most frequently the cleaning is carried out by the combination of processes (1) and (3) only. In any case, the dust in the gas should be reduced down to about 0·01 gram per cub. metre, and the temperature to 18°–20°, before delivery to the engine. The power expended in cleaning the gas to this degree amounts to between 5 and 6 p.c. of that generated by its explosion in the engine cylinder.

Processes of dry-cleaning (*e.g.* the Beth-Halberg system, in which the gas is filtered through a special fabric) have been successfully developed within recent years; but probably the best solution of the cleaning problem lies in some electrostatic system whereby the whole of the dust can be successfully eliminated with a minimum expenditure of energy and without using water or sensibly cooling the gas. A description of the Lodge Electrostatic Process for gas-cleaning as recently installed at Skinningrove Ironworks is given in a paper by A. Hutchinson and E. Bury, in Journ. Iron & Steel Inst. cii. (1920), p. 65.

Water gas. The need of a cheap gaseous fuel of high calorific intensity for certain industrial purposes (*e.g.* steel welding) has led to the utilisation of the well-known endothermic interaction of steam and incandescent carbon at high temperatures. For such a process to be continuous, heat would have to be transmitted from an external source through the walls of the reaction chamber or retort, which would necessarily be constructed of refractory material of low conductivity. As such procedure would certainly be very uneconomical, all idea of it has been abandoned in favour of an intermittent process, in which a bed of fuel (usually coke) is alternately blown with (1) air, until the mass attains a sufficiently high temperature, and (2) with steam, so long as the high temperature interaction $C + H_2O \rightleftharpoons CO + H_2$ can proceed without undue occurrence of the low temperature interaction $C + 2H_2O \rightleftharpoons CO_2 + 2H_2$

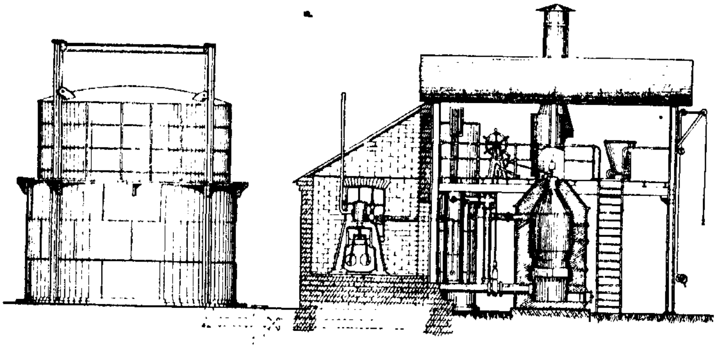


Fig. 13.

The use of water gas was first introduced in the United States about the year 1875, as the result of the pioneering efforts of J. S. C. Lowe, but it was not until 1888 that the British Water Gas Syndicate installed the first plant in Great Britain at the Leeds Forge. This plant embodied the now obsolete idea of, during the 'air blow,' manufacturing a low grade 'producer gas' (a mixture of CO_2, CO, and N, in which CO was the predominating carbon constituent) for furnace purposes by blowing a thick fuel bed with an air blast at moderate pressure. This operation was alternated with the usual 'steam blow' for the production of 'water gas.' The 'air blow' occupied 10 minutes, and the 'steam-blow' only 4 minutes, and each ton of gas coke yielded about 34,000 cub. ft. of 'water gas,' and about 140,000 cub. ft. of 'producer gas,' some 25 p.c. only of the carbon in the fuel appearing in the 'water gas.'

Some ten years later the process was much improved by Dellwik and Fleischer, who proposed, during the air blow, to heat up a comparatively thin bed of fuel as rapidly as possible by means of a blast supplied in such quantity as to burn the carbon as completely as possible to the dioxide. In the Dellwik-Fleischer system (Figs. 13 and 14), the generator is of cylindrical section with a fire-brick lining encased in a steel shell. The fuel bed rests on a flat bar grate on a level with which are clinkering bars, and below which are doors for the removal of ashes. The air blast always enters the fuel bed from below through a valve, and the products of the 'air blow' leave the generator by the central stack valve, through which also the fuel is charged from a small hopper waggon. During the 'steam blows' superheated steam from a boiler working at a pressure of 150–160 lbs. per sq. in. is blown through the incandescent fuel bed in either an upward or a downward direction, the direction being reversed in each successive blow. Accordingly, there is one 'water-gas' outlet at the top of the generator, and another below the grate, each provided with a valve leading to the annular 'superheater,' which serves to effect a heat exchange between the outgoing hot gas and the incoming steam blast, thus superheating the latter. At the bottom of the 'superheater' is a water seal through which the gas passes onwards to a coke scrubber, where it is cooled and cleaned from dust by means of a water spray; from thence the cold gas passes into a holder. The various valves of the generator are operated by an interlocking gear which makes it impossible for the operator to make a mistake or get an explosive mixture in any part of the plant. A set of water gauges and a test flame on the

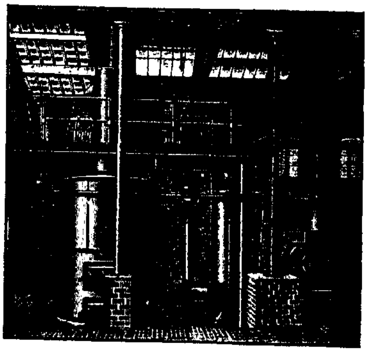


Fig. 14.

operating platform indicate the working conditions in the generator at any moment and also the quality of the gas during the 'steam blow.' Towards the end of the 'steam blow,' when the temperature of the fuel has fallen below the point at which the low temperature interaction $C+2H_2O \rightleftharpoons CO_2+2H_2$ comes seriously into play, the steam and gas valves are shut off, the stack and air valves being simultaneously opened, for the commencement of the 'air blow.' Each 'air blow' lasts about 1 minute, and the subsequent 'steam blow' about 4 minutes. With an average quality of gas coke the plant will produce about 32 cub. ft. at 0° and 760 mm. of water gas per lb. of carbon charged into the generator, which means that as nearly as possible 50 p.c. of the carbon is converted into water gas. The average composition of the gas is 4·0 CO_2, 43·0 CO, 49·0 H, 0·5 CH_4, and 3·5 p.c. N, and its calorific value about 320 gross and 290 net B.Th.Us. per cub. ft. at 0° and 760 mm. The *ratio* of the net calorific value of the gas to that of the coke charged into the generator is about 0·60.

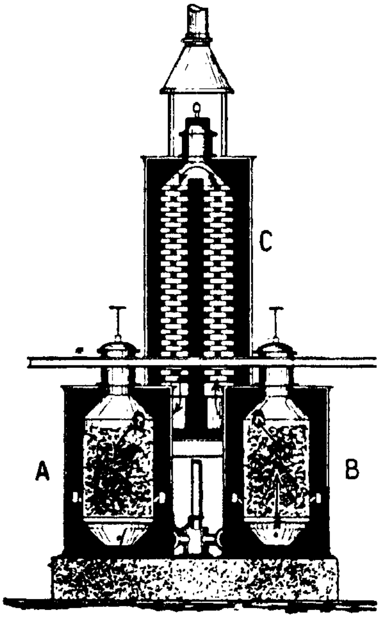


FIG. 15.

Another system of water-gas making is that embodied in the Kramers and Aarts patents (the 'K and A' system), according to which two generators, A and B (Figs. 15, 16, and 17), connected through a double 'regenerator,' C, are operated in parallel during the 'air blow' and in series during the 'steam blow,' somewhat as follows:—

During the 'air blow' the fires (5–6 feet in thickness) in both regenerators are simultaneously blown in parallel by a powerful blast, which is introduced from below each fire. The hot products (CO_2, CO, and N), on leaving the top of the generators, pass upwards through the 'double regenerator,' a cylindrical structure filled with fire-brick chequer work and divided vertically into two chambers or compartments by a central fire-brick wall. As the hot products enter in parallel streams at the base of one or other of the two chambers, they meet a secondary air supply sufficient to burn completely all the CO which they may contain. The chequer work in the chambers absorbs part of the heat of the burnt gases which eventually make their exit into the outer atmosphere through the stack valve D at the top of the double regenerator. As soon as the fires in the two generators have attained the necessary high temperature, the air and stack valves are shut, and the steam valve simultaneously opened. The steam, entering the base of the first generator, traverses the fire contained therein in an upward direction.

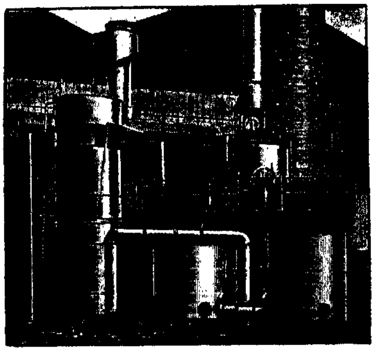
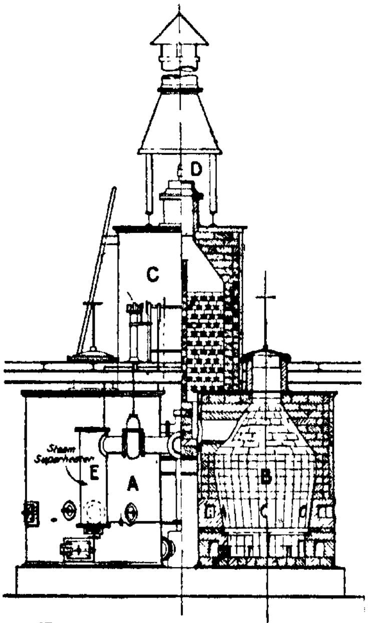


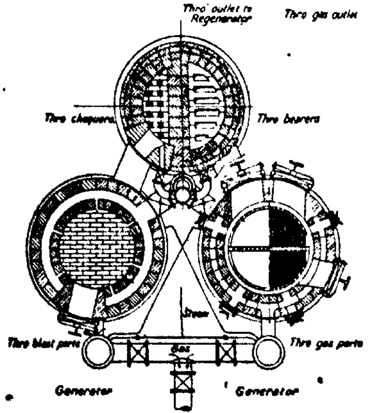
FIG. 16.

The products (CO_2, CO, H, and some undecomposed steam) passing out at the top traverse in a ∩ direction the two chambers of the 'double regenerator,' after which they enter, in a highly 'superheated' condition, the top of the second generator, through which they pass in a downward direction. In this way, it is claimed, the gases, just prior to leaving the system, come into contact with a bed of highly incandescent carbon, the temperature of which has not been sensibly lowered by the main endothermic steam-carbon interaction, which principally occurs in the first of the two generators. In alternate 'steam blows,' the direction of the steam and gases is reversed, in order to ensure the maximum of uniformity in the working conditions. The plant is operated by means of an interlocking valve gear, which prevents mistakes on the part of the workman. The hot gas produced passes from the bottom of the second generator upwards first of all through the annular 'steam superheater' E (Fig. 17), whereby part of its sensible heat is transmitted to the in-going steam blast, and then through a coke scrubber, where it is cleaned and cooled by a downward water spray. The process works smoothly and is very efficient, the average duration of each air blow being about 70 seconds, and of each steam blow about

5 minutes. The yield of gas, from an average gas coke, is nearly 38 cub. ft., at 0° and 760 mm., per lb. of carbon charged into the generator, about 60 p.c. of which appears in the 'water gas.' The composition of the gas is 3·75 CO_2, 43·70 CO, 45·1 H, 0·5 CH_4, and 0·95 N, its calorific value being about 310 gross and 285 net B.Th.Us. per cub. ft. at 0° and 760 mm. The ratio of the net calorific value of the water gas to that of the coke charged into the generators is about 0·70.



ELEVATION. SECTION



SECTIONAL PLAN.

FIG. 17.

With coke at *12s.* per ton, the pre-war cost of making 'blue water gas,' including fuel, wages, interest, and depreciation, was about *4d.* per 1000 cub. ft., which was equivalent to coal gas at about *8d.* per 1000 cub. ft. Post-war costs cannot well be estimated until prices of coal and labour are more stabilised, but they are now (1921) probably not less than 3 to 4 times the pre-war figure.

The most important industrial application of water gas is undoubtedly steel-plate welding, and a large industry has grown up, especially in Germany, for the manufacture of welded steel tubes of large dimensions. The overlapping joint to be welded is heated simultaneously from both sides by special burners (Fig. 18) fed with both water gas and air under pressure, which on mingling produce aërated flames of great heating power. As soon as the joint attains the proper welding heat, it is quickly passed through special rolls which bring about a perfect weld.

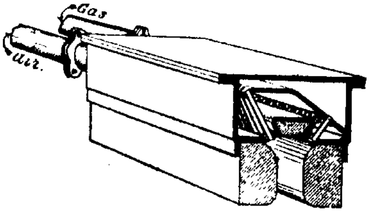


FIG. 18.

Water gas is also used for mixing with ordinary town coal gas, but for this purpose it usually first of all undergoes a process of 'carburetting.' (For the production of 'Carburetted Water gas,' *see* GAS, COAL; *also* GAS, WATER.)

The combustion of gaseous fuels. The following table, relating to the various forms of gaseous fuels described in this article, may be found useful for comparative purposes; the figures for calorific values are approximate only:

Gas	Net cal. value B.Th.Us. per cub. ft. at 0° and 760 mm.	Vol. air required to burn 1 vol. of gas	Vol. gas + air required per 100 B.Th.Us. cub. ft.	Vol. products incl. H_2O per 100 B.Th. Us. cub. ft.
Blast-furnace gas . .	100	0·715	1·715	1·565
Producer gas	150	1·216	1 480	1·357
Water gas .	290	2·200	1·100	0·953
Coal gas .	590	5·440	1·100	1·050

For information as to the present state of science in gaseous combustion, *see* article on FLAME (this vol. p. 206) and also reports by W. A. Bone to the British Association, Sheffield, 1910 and 1915. Attention is also drawn to the recent revival of the subject of 'surface combustion' by W. A. Bone and C. D. McCourt (*vide* Proc. Roy. Institution, xxi. No. 108 (1917), pp. 41–62; and Howard Lectures, Roy. Soc.

Arts, 1914) whereby numerous economies in the industrial application of gaseous fuels (including steam raising by means of blast furnace gas, producer gas, or surplus gas from by-product coking plants) may be realised. During the war the 'Bonecourt' system was successfully developed for large gas-fired boilers (with 'superheat') for power stations, and it has also been extensively applied to industrial furnaces in America. Also, their method of 'diaphragm heating' by radiation has recently been successfully applied in the manufacture of confectionery, etc. W. A. B.

FUKUGI. The Japanese dyestuff fukugi (botanical origin unknown) has, at least until recently, been employed to a considerable extent as a mordant dyestuff in Japan. It consists of the wood of a tree, which, when ground, forms an almost colourless powder, the extract of which is sold in the form of brittle rectangular cakes of a yellowish-brown colour.

Fukugetin $C_{17}H_{12}O_6$, the colouring matter, forms minute canary-yellow prismatic needles, melting at 288°–290° (Perkin and Phipps, Chem. Soc. Trans. 1904, 85, 58). It dissolves in alkaline solutions with a yellow colour and gives with alcoholic lead acetate an orange-yellow precipitate, and with alcoholic ferric chloride a brown-black coloration.

Crystalline acetyl and benzoyl derivatives of this colouring matter could not be obtained, but the *bromine compound* $C_{17}H_{10}O_6Br_2$, minute flat needles, m.p. 280°, is readily prepared by the action of bromine on fukugetin in the presence of acetic acid.

Fukugetin dyes mordanted fabrics shades which are almost identical with those given by luteolin:

Chromium	*Aluminium*	*Tin*	*Iron*
Dull orange-yellow	Orange-yellow	Bright yellow	Olive-brown

and resembles this colouring matter in that its alkaline solution is not oxidised on exposure to air. By fusion with alkali, fukugetin gives *phloroglucinol* and *protocatechuic acid.*

The dyeing properties of 'fukugi' are analogous to those of weld. The similarity in shade, indeed, is so marked that, except in point of strength—for fukugi is a stronger dye than weld—it is impossible to distinguish between them. A. G. P.

FULLER'S EARTH. (Fr. *Terre à foulon*; Ger. *Walkerde.*) A term applied to a variety of clay-like materials which possess in common the property of absorbing grease and oil, and hence are used by fullers for cleansing woollen goods. They vary in colour with dull shades of grey, yellowish, bluish, or greenish, and are soft, with an earthy appearance. They are greasy and unctuous to the touch, and do not adhere to the tongue. When a lump of the dried earth is placed in water, it presents a very curious appearance as it crumbles down to a fine powder; and is not plastic like ordinary clays. Mineralogically they appear to be mixtures; some approximate to kaolinite ($Al_2O_3{\cdot}2SiO_2,2H_2O$) in composition, and many may be referred to the 'smectite' of A. Breithaupt (1841), a greenish-grey clay from Cilly in Styria. A microscopical examination of English fuller's earth, made by G. P. Merrill (The Non-metallic Minerals, 1904), showed the presence of colourless and greenish-yellow particles with very feeble birefringence, ranging from 0·002 to 0·07 mm. in diameter: very little quartz could be detected, although the presence of free silica is suggested by the analyses. The chemical composition varies widely, and is, in fact, no guide to the commercial value of the material, which depends rather on the physical state of aggregation. Sp.gr. 1·75–2·5.

The following analyses are of: I, smectite from Cilly, Styria (Jordan, 1849); II, bluish-grey fuller's earth from Nutfield, Surrey (P. G. Sanford, Geol. Mag. 1889, 456, 526), on material dried at 100° with a loss of 27·47 p.c. water; 13·33 p.c. of all the solid constituents except silica, are soluble in acid; III, yellowish fuller's earth from Nutfield, Surrey (P. G. Sanford, 1889), on material dried at 100° with loss of 29·56 p.c. water; 10·73 p.c. solids, soluble in acid; IV, from Fairborn, South Dakota; V, from south-east of River Junction, Florida; VI, from Decatur Co., Georgia (anal. IV–VI by E. J. Riederer, quoted by H. Ries, 17th Ann. Rep. U.S. Geol. Survey, 1896, iii. 880).

	I.	II.	III.	IV.	V.	VI.
SiO_2	51·21	62·81	59·37	58·72	50·70	67·40
Al_2O_3	12·25	6·92	11·82	16·90	21·07	10·08
Fe_2O_3	2·07	3·78	6·27	4·00	6·88	2·49
CaO	2·13	7·40	6·17	4·06	4·40	3·14
MgO	4·89	2·27	2·09	2·56	0·30	4·00
K_2O	·	0·74	0·84	2·11	—	—
Na_2O	—	—	—			
NaCl		0·05	0·14	—	—	—
P_2O_5	—	0·27	0·14	—	—	—
SO_3	—	0·05	0·07	–	—	—
H_2O(comb.)	27·89	15·57	13·19	8·10	9·60	5·61
Moisture		—	—	2·30	7·90	6·28
	100·44	99·86	100·10	98·75	100·85	99·15

Fuller's earth occurs as beds in sedimentary rocks belonging to various geological periods, ranging from the Silurian to the Eocene. The most important deposit in England is a bed 8–12 feet in thickness, lying between sandstones in the Lower Greensand division of the Cretaceous system. This is worked in open pits at Nutfield and Redhill in Surrey. Nearer the surface, where oxidised, it is yellowish, but lower down it is bluish in colour. In Somersetshire, Gloucestershire, and Dorsetshire, the 'fuller's earth formation' of geologists, lying between the limestones of the Great Oolite and the Inferior Oolite, consists of a thick deposit of clays and marls, with beds 2–3 feet in thickness of fuller's earth of good quality. This was formerly extensively worked for use in the cloth mills of the west of England, but now is obtained only on the Downs to the south of Bath. Still smaller quantities are yielded by the Lower Greensand strata near Woburn in Bedfordshire.

For many years the English fuller's earth was considered the best, and until recently large quantities were exported to America. Deposits have now been opened up at several places in the United States, chiefly in Florida, and to a lesser extent in Georgia, Alabama, Arkansas, and California. In Gadsden Co., Florida, it occurs as a bed 4–12 feet in thickness in bedded clays and sandy clays of Oligocene (Tertiary) age. Small outputs are also recorded from India and Australia (Wingen, New South Wales).

The English output amounts to about 15,000 tons per annum, whilst double this quantity is now obtained in America. The price at the pits ranges from 25s. to 2l. per ton. The earth as dug is dried, crushed, and passed through fine sieves of silk or bronze gauze.

Although still used for cleaning cloths, scouring yarns, and washing woollens and fine-dyed goods, fuller's earth now finds a more extensive use in the refining of oils,[1] grease, and lard. Mineral oils are decolorised and clarified by allowing the oil to percolate through long cylinders filled with coarser fuller's earth. Vegetable oils, such as cotton-seed oil, are warmed, stirred with 5 10 p.c. earth, and filtered through bags. The main points to be determined in the valuation of the earth in the oil industry are the relative bleaching power and the quantity of oil absorbed. For a method of testing fuller's earth for these factors, *see* Richert, J. Ind. and Eng Chem. 1917, 9, 599; Analyst, 1917, 340. Fuller's earth has also been used in the manufacture of pigments for printing wall papers. Small quantities of the finest grades are used for toilet preparations.

References.—J. T. Porter, Properties and Tests of Fuller's Earth, U.S. Geol. Survey, Bull 315, 1907; H. Ries, Clays, their Occurrence, Properties, and Uses, 2nd ed., New York, 1908; C. L. Parsons, U.S. Bureau of Mines, Bull 71, 1913. Fuller's Earth, Imp. Min. Res. Bur. London 1920. L. J. S.

FULMARGEN. A form of colloid silver.

FULMINIC ACID (Ger. *Knallsäure*) C:NOH The acid has not been obtained in a free state Scholvein (J. pr. Chem. [2] 32, 461) obtained an ethereal solution of the acid by treating sodium fulminate with dilute sulphuric acid, keeping the mixture cool and dissolving the yellow oil thus obtained in ether. Wieland and Hess (Ber. 1909, 1346) have confirmed this statement, and found that the acid rapidly polymerised to metafulminuric acid (*v. infra*). Howard first showed that when silver nitrate or mercuric nitrate was treated with alcohol and excess of nitric acid, a crystalline, detonating precipitate, fulminating silver or fulminating mercury, was obtained. Analyses of these substances (Liebig, Ann. Chim. [2] 24, 298; Annalen, 24, 546; Gay-Lussac, Ann. Chim. [2] 25, 285; Divers and Kawakita, Chem Soc. Trans. 1884, 17) show that they are salts of an acid possessing the formula HCNO. The constitution of this acid has given rise to much discussion. Berzelius wrote fulminating silver as

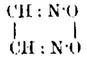
$$Ag_2O{\cdot}(AgN)_2{\cdot}C_4N_2O_3$$

This formula accounted for the fact that in many of its reactions only half of the metal is separated, also that the double fulminate of potassium and silver detonates as violently as fulminating silver itself, the detonation being attributed to the decomposition of the compound AgN. Laurent and Gerhardt next proposed the constitution $C_2N(NO_2)Ag_2$, assigning the explosive nature of the body to the presence of a nitro group, and the subsequent experiments of Kekulé (Annalen, 101, 200; 105, 279) and Schischkoff (*ibid.* 101, 213) apparently confirmed this view.

Later Kekulé formulated fulminic acid as nitroacetonitrile $CH_2(NO_2)CN$. He based this formula chiefly on two reactions which fulminic acid undergoes. When mercuric fulminate is treated with sulphuretted hydrogen, ammonium thiocyanate is produced, and with aqueous hydrochloric acid, hydroxylamine is the main product. The production of ammonium thiocyanate suggests that in fulminic acid there is a (CN) group, and that the two nitrogen atoms are in different states of combination, which facts fit in with the formula proposed. But of the two nitrogen atoms only one is represented as oxidised and capable of conversion into hydroxylamine, whereas Divers and Kawakita (Chem. Soc. Trans. 1884, 16) have shown that both atoms of nitrogen are so convertible. Schischkoff (Bull. Soc. chim. 1860, 294) doubled Kekulé's formula. Steiner proposed

$$HO{\cdot}N:C:C:N{\cdot}OH$$

as the correct configuration (Ber. 1876, 779); and Scholl formulated fulminic acid as glyoxime peroxide



$$\begin{array}{l} CH:N{\cdot}O \\ \vert \qquad\quad \vert \\ CH:N{\cdot}O \end{array}$$

In 1894 Nef found that on treating sodium nitromethane with mercuric chloride, mercuric fulminate was produced, and, moreover, that sodium nitromethane, on treatment with aqueous hydrochloric acid, decomposed into formic acid and hydroxylamine, as does fulminic acid (*v. supra*). On these grounds Nef formulated fulminic acid as carbonyl monoxime C:NOH, and represented the production of mercuric fulminate from nitromethane as follows:—

$$CH_3NO_2 \xrightarrow{\text{Alkali}} \underset{\text{Pseudo-modification.}}{CH_2{:}NO{\cdot}ONa} \xrightarrow{HgCl_2} \underset{\text{Unstable.}}{(CH_2{:}NO{\cdot}O)_2Hg} \xrightarrow{-H_2O} (C{:}NO)_2Hg$$

The explosive character of the fulminates is accounted for by the presence of bivalent carbon in the molecule. It was an old observation, first noticed by Liebig, that when mercuric fulminate was treated with hydrochloric acid of a certain strength, prussic acid was evolved, and this fact was long used to support the nitroacetonitrile formula for fulminic acid. But Nef showed that the compound formed was not prussic acid, but chloroformoxime, a compound possessing an odour similar to that of prussic acid.

$$C:NONa+2HCl=CHCl:NOH+NaCl$$

Hydrochloric acid converts chloroformoxime into hydroxylamine hydrochloride; sodium hydroxide regenerates a fulminate (Nef, Annalen, 280, 263, *et seq.*). Moreover, nitroacetonitrile has been prepared by removing the elements of water from methazonic acid $C_2H_4O_2N_2$, and is found to have none of the characteristic properties of fulminic acid (Steinkopf and Bohrmann, J. pr. Chem. 1910, [ii.] 81, 97, 193; Ber. 1908, 1044). Scholl (*ibid.* 1899, 3492) applied Friedel and Craft's reaction to fulminic acid, and found that on gently warming mercuric fulminate with benzene, aluminium, and aluminium chloride, benzaldoxime is produced, a further confirmation of Nef's carbonyloxime formula. Angelico (Chem. Zentr. 1901, ii. 404) obtained fulminic acid by treating a solution of mercuric nitrate in excess of dilute nitric acid with a concentrated solution of malonic acid and a few drops of sodium nitrite solution. The course of the reaction is as follows :—

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[1] The selective absorption of fuller's earth is greater for oils of higher sp.gr. and viscosity and for unsaturated hydrocarbons and sulphur compounds (J. E. Gilpin and O. E. Bransky, Amer. Chem. J. 1910, 44, 251).

$$\mathrm{CH_2(COOH)_2 \rightarrow C:NOH(COOH)_2}$$

*iso*Nitrosomalonic acid.

$$\mathrm{\rightarrow C(:NOOH)(COOH)_2 \rightarrow CH(:NOOH)(COOH)}$$

*iso*Nitromalonic acid. *iso*Nitroacetic acid.

$$\mathrm{\rightarrow CH_2:NOOH \rightarrow C:NOH}$$

*iso*Nitromethane.

Wieland and Semper (Ber. 1906, 2522) have shown that phenylmethylnitrolic acid readily decomposes into nitrous acid and the unstable benzonitrile oxide.

$$\mathrm{C(C_6H_5)\Big<{}^{NOH}_{NO_2} \rightarrow HNO_2 + C_6H_5{\cdot}C\vdots N:O}$$

Hence, if a similar decomposition occurs in the case of methyl nitrolic acid, the hitherto unknown nitrile oxide $\mathrm{H{\cdot}C\vdots N:O}$ or the products of its decomposition would be obtained. Wieland (*l.c.*) has shown that the products of the decomposition of methylnitrolic acid are fulminic acid, formic acid, and hydroxylamine, the decomposition being analogous to that of chloroformoxime. The unstable nitrile oxide is probably formed first and then undergoes an isomeric change into fulminic acid.

Wohler (Ber. 1905, 1351) has determined the molecular weight of fulminic acid by means of the sodium salt, which can be prepared in a pure anhydrous state by the action of sodium amalgam on mercury fulminate suspended in alcohol. The numbers obtained by the cryoscopic method and by determining the equivalent conductivities of dilute solutions correspond closely with the numbers required for the monomolecular formula C : NONa.

In the ordinary method of preparing fulminates by the oxidation of ethyl alcohol, the following changes are supposed to occur (Wieland, Ber. 1907, 418) :—

$$\mathrm{CH_3{\cdot}CH_2{\cdot}OH \rightarrow CH_3CHO \rightarrow CH(:NOH){\cdot}CHO}$$

Aldehyde *iso*Nitrosoacetaldehyde.

$$\mathrm{\rightarrow CH(:NOH){\cdot}COOH \rightarrow NO_2{\cdot}C(:NOH){\cdot}COOH}$$

*iso*Nitrosoacetic acid. *iso*Nitrosonitroacetic acid.

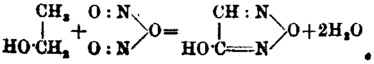
$$\mathrm{\rightarrow NO_2{\cdot}C(.NOH)H \rightarrow C:NOH}$$

Methylnitrolic acid.

The experimental evidence in favour of the above hypothesis is as follows: Wieland and Theodorovits (Ber. 1905, 1345) found aldehyde to be a more suitable agent than alcohol for the preparation of fulminates, the formation of methylnitrolic acid from *iso*nitrosoacetic acid has been accomplished by Ponzio (Chem. Soc. Abstr. 1903, i. 453), Wieland has prepared mercuric fulminate from methylnitrolic acid (*v. supra*); and lastly by treating fulminic acid with nitrous acid, Palazzo (Chem. Soc. Abstr. 1907, i. 489) has obtained methylnitrolic acid as one of the products of the reaction.

The older view of Kekulé as to the constitution of fulminic acid has now been finally abandoned, and the carbonyl oxime formula of Nef has taken its place.

Hodgkinson (J. Soc. Chem. Ind. 1918, 37, 190, T) has pointed out that mercury fulminate cannot be formed in the absence of nitrous acid or a mixture of nitric oxide and nitrogen peroxide; he, therefore, represents the formation and constitution of fulminic acid by the equation :



Mercuric fulminate or fulminating mercury $\mathrm{(C:NO)_2Hg}$. To prepare this substance on a small scale, 3 parts of mercury are dissolved in 36 parts nitric acid of sp.gr. 1·34, without warming. The solution is then poured into a flask capable of containing 18 times the quantity, in which there has been placed 17 parts alcohol of from 90–92 volumes p.c. The liquids are well mixed, poured back into the first vessel, which is of the same size, shaken to absorb nitrous fumes, and the whole then allowed to stand. In a short time gas is given off and a highly refracting liquid separates at the bottom of the flask. On shaking the flask to mix this liquid with the rest, the whole becomes black, metallic mercury separates, and a violent reaction takes place, which is moderated by the gradual addition of 17 parts of alcohol. Crystals of mercuric fulminate separate on cooling (Liebig).

For methods of production on the large scale, *see* EXPLOSIVES.

Mercuric fulminate may also be produced by using mercuric oxide for mercury in the above preparation; by boiling silver fulminate with mercury and water, or by precipitating the zinc salt with mercuric chloride. Wöhler and Theodorovits (Ber. 1905, 1345) state that mercuric fulminate is also formed when mercuric nitrate in dilute nitric acid is mixed with methylal, acetal, or lignone obtained by the dry distillation of wood, but the acid must contain nitrous fumes.

For its preparation from oximino acetic acid, *see* Wieland, Ber. 1910, 43, 3362.

It crystallises from hot water in white or greyish silky needles of sp.gr. 4·42; its gravimetric density varies from 1·3 to 1·6, depending upon the size of the crystals; its formula is $\mathrm{(C:N{\cdot}O)_2Hg,\tfrac{1}{2}H_2O}$; by carefully regulating the temperature and the amount of alcohol, it can be obtained anhydrous. It is nearly insoluble in cold water, but soluble in alcohol, pyridine, potassium cyanide, and, with decomposition, in sodium or ammonium thiosulphate solution. Nicolardot and Boudet (Bull. Soc. chim. 1919, 25, 119) employ the last-named aqueous solutions in 5 p.c. strength to dissolve mercury fulminate for purposes of analysis, the impurities it commonly contains remaining undissolved.

When heated to 180° or when forcibly struck, mercuric fulminate detonates with great violence. The electric spark, or the spark from flint and steel, or contact with nitric or sulphuric acids also bring about explosive decomposition. Large crystals are more sensitive to impact than small ones. When moist it may be handled without danger, and when heated to 100° it does not explode if the crystals contain no enclosed mother liquor. The disruptive force of the explosion within a small space is greater than that of gunpowder, but too sudden for its use in guns. The pressure exerted by the gases evolved in the decomposition of the fulminate is less than that caused by the explosion of an equal weight of guncotton, the greater action of the former being attributed to the density of the compound and the great rapidity of the decomposition. Fulminate of mercury is used in the manufacture of percussion caps and of the various detonators used for exploding guncotton, dynamite, and other nitro-glycerin compounds (*v.* EXPLOSIVES)

Concentrated hydrochloric acid reacts with perfectly dry mercuric fulminate to produce formic acid and hydroxylamine hydrochloride. Thus:

$$C:NOH+2H_2O=H{\cdot}COOH+NH_2{\cdot}OH$$

If the acid be dilute and of a certain strength, chloroformoxime is produced (*v. supra*).

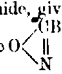
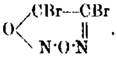
Moderately dilute sulphuric acid decomposes mercuric fulminate without explosion; hot nitric acid converts it into mercuric nitrate, acetic acid, and carbon dioxide. If sulphuretted hydrogen be passed through ether in which mercuric fulminate is suspended, ammonium thiocyanate is formed (*v. supra*); but if the system is kept free from moisture, nitrothioacetamide

$$CH_2(NO_2)CS{\cdot}NH_2$$

is also produced, and is decomposed by a further quantity of sulphuretted hydrogen into ammonium thiocyanate, oxalic acid, and sulphur (Steiner, Ber. 1874, 1244; 1875, 518; 1879, 779). Heated with aqueous ammonia, mercuric fulminate yields urea, guanidine, and complex nitrogenous substances; with alcoholic ammonia fulminuric acid is the main product (Steiner).

Potash, lime, and strontia decompose mercuric fulminate on boiling, with the separation of mercuric oxide and the formation of double salts, which detonate on percussion (Liebig).

Finely divided zinc, copper, or silver (the last in contact with platinum) displace mercury from the fulminate, forming salts of zinc, copper, or silver. (For the action of mercuric fulminate on various metals and alloys *see* Langhans, Zeitsch. ges. Shiess. u Sprengstoffen. 1921, 16, 108.) Mercuric fulminate readily forms double salts with potassium cyanide and potassium and ammonium thiocyanates (Steiner).

Bromine reacts with mercuric fulminate to produce first of all the unstable additive compound $(CBr_2:N{\cdot}O)_2Hg$, which loses mercuric bromide, giving the unstable bromoformonitrile oxide , two molecules of which polymerise to form dibromofuroxan . Chlorine reacts similarly, but the oxidising power of the halogen is so strong as to completely destroy the molecule, with the evolution of carbon dioxide (Wieland, Ber. 1909, 4192).

For the electrolytic estimation of mercury in mercury fulminate, *see* Losanitsch, Monatsh. 1914, 35, 307.

Silver fulminate, *Fulminating silver*

$$C:NOAg$$

In preparing this substance 1 part silver is dissolved in 20 parts nitric acid of sp.gr. 1·36 and 27 parts of 86 p.c. spirit of wine added, and the whole gently heated till it froths up. The liquid is then removed, and 27 parts or more of spirit added in order to moderate the action. Silver fulminate separates out on cooling (Liebig).

Silver fulminate is not formed, as was stated by Liebig (Annalen, 5, 287), when nitrogen trioxide is led into an alcoholic solution of silver nitrate (Divers and Kawakita, Chem. Soc. Trans. 1884, 27), and is only produced by the energetic oxidation of alcohol by nitric acid in presence of silver nitrate. Great caution must be exercised in the preparation of this substance. Capacious vessels must be used, so that the liquid may not boil over, as in that case the salt might dry on the outside and then explode; all flame must be kept at a distance, lest the vapours should take fire; and the mixture should be stirred with wooden rods, not with glass rods or other hard bodies. When dry it should be transferred on paper shovels, and kept in paper or cardboard vessels, loosely covered, to prevent explosion from the friction of stoppers or lids.

Silver fulminate crystallises in white opaque glistening needles, scarcely soluble in water, and having a bitter metallic taste. Given in certain doses, it produces violent convulsions (Pagot-la-Forêt), while in doses of 0·3 gram it acts as a narcotic (Ittner).

Silver fulminate is an exceedingly dangerous body, as it explodes much more violently than the mercury salt, by the action of heat, by the electric spark, by friction or percussion, or by contact with oil of vitriol. It even explodes in the moist state, sometimes under water, by friction with a glass rod. It may be rubbed to powder in a mortar with the finger or with a cork. The light accompanying the explosion, which is best seen in the dark, is reddish-white with a tinge of blue (Liebig). When ignited under a pressure of about 2 or 3 mm., it burns slowly with a visible flame. If silver fulminate be thrown into a bottle containing chlorine, it deflagrates before it reaches the bottom, and does not fracture the bottle (E. Davy). Silver fulminate dissolves in hot aqueous ammonia, and the solution, on cooling, deposits crystalline grains of ammonium silver fulminate

$$(C:NO_2)(NH_4)Ag$$

This salt is sparingly soluble in water, and explodes with much greater violence than the silver salt, even under liquid, when touched with a glass rod (Liebig). Aqueous solutions of the hydroxides of the metals of the alkalis or alkaline earths, or of the sulphides or chlorides of the alkalis, yield similar double salts when boiled with silver fulminate. Copper or mercury can displace silver wholly or in part from silver fulminate. Zinc, even on boiling for several days, displaces only half of the silver, forming silver-zinc fulminate. The normal zinc salt is prepared by the action of zinc on mercuric fulminate. By acting on this salt with baryta water, and exactly precipitating the barium from the zinc barium fulminate thus produced with sulphuric acid, zinc hydrogen fulminate is obtained. By saturating this salt with metallic bases, many double salts of zinc fulminate are obtained.

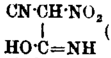
Cadmium fulminate $Ca(CNO)_2$ is a white powder, stable when dry, but readily decomposed by water, in which it is very soluble. It is one of the most violent explosives, and is nearly as sensitive to shock and heat as mercury fulminate. *Thallous fulminate* becomes yellow on exposure to light, and is the most susceptible of all known fulminates to shock and increased temperature, but the heat of detonation is not high, and its explosion is not violent. *Cuprous fulminate* is insoluble in water, and is almost as violently explosive as cadmium fulminate, although not so sensitive to shock (L. Wöhler and Martin, Ber. 1917, 50, 586).

Fulminic acid gives rise to a series of polymerisation products. If mercuric fulminate is boiled with ammonium chloride, a salt of fulminuric acid is formed, as was discovered by Liebig. When the ethereal solution of fulminic acid is allowed to stand, metafulminuric acid, a triple polymer, is produced. When metafulminuric acid is warmed with water, it yields cyan*iso*nitrosoacetohydroxamic acid, and the latter can be converted into the *iso*fulminuric acid of Ehrenberg, the constitution of which is still unknown. Finally, on long standing metafulminuric acid changes into the β-*iso*fulminuric acid of Scholvein.

FULMINURIC ACID $C_3H_3N_3O_3$. This compound was discovered independently by Liebig (Annalen, 95, 282) and Schuschkoff (*ibid.* 97, 53; 101, 213). It is produced by boiling a solution of a metallic chloride or iodide with water and mercuric fulminate

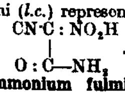
$$4C:NOH+H_2O=C_3H_3N_3O_3+CO_2+NH_3$$

30–75 grams of well-washed mercuric fulminate are boiled with 700–800 c.c. of water, 60 c.c. of a saturated solution of ammonium chloride are then added, and the whole heated to the boiling-point. As soon as a yellow deposit of oxydimercuric ammonium chloride separates, the flame is removed, and ammonia added till all the mercury is precipitated. On filtering, evaporating the filtrate, and recrystallising the first crop of crystals, pure ammonium fulminurate is obtained. By converting this into the basic lead salt by treating with lead acetate and then precipitating with sulphuretted hydrogen, an aqueous solution of fulminuric acid is obtained. This, on evaporation and standing in a warm place, solidifies to an indistinctly crystalline mass, which, dissolved in alcohol, deposits on evaporation colourless prisms of fulminuric acid. The potassium or ammonium salt may be converted into the silver salt, which may be decomposed by hydrochloric acid, yielding free fulminuric acid. Another method of preparing fulminuric acid is that of Ulpiani (Gazz. chim. ital. 1905, iii. 357). Succinamidodinitrosoperoxide, obtained by the action of fuming nitric acid on ethylacetoacetate and subsequent treatment with concentrated ammonia, yields an acid which Ulpiani has proved to be identical with the fulminuric acid of Liebig, and also β-*iso*fulminuramide. The latter yields β-*iso*fulminuric acid on hydrolysis. Fulminuric acid decomposes on heating with a slight deflagration at 145° (Steiner, Ber. 1872, 381), and by heating with dilute acid or alkalis decomposes into oxalic acid, ammonia, and carbon dioxide. It appears to be monobasic. The constitution of fulminuric acid is still uncertain. Nef regards it as nitrocyanoacetamide



$$\begin{array}{l} CN\cdot CH\cdot NO_2 \\ \quad | \\ HO\cdot C{=}NH \end{array}$$

(Annalen, 280, 329); while Ulpiani (*l.c.*) represents it as *iso*nitrocyanoacetamide



$$\begin{array}{l} CN\cdot C:NO_2H \\ \quad\ | \\ O:C{-}NH_2 \end{array}$$

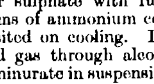
Ammonium fulminurate forms anhydrous monoclinic crystals, which blacken on heating and give off hydrocyanic acid, ammonia, and cyanic acid, which latter partially unite to form urea (Liebig).

Potassium fulminurate. To prepare this salt two parts of mercuric fulminate are gradually added to a saturated solution of one part of potassium chloride, and the mixture gently boiled till the whole is dissolved. The liquid is filtered through a hot funnel from a yellowish precipitate which appears, and the compound of mercuric oxide and potassium fulminurate, which separates in the filtrate, is freed from mercury by sulphuretted hydrogen. On recrystallising from water, potassium fulminurate separates in long glistening prisms, which decompose with incandescence when heated to 225° (Schischkoff).

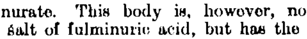
Silver fulminurate may be obtained by heating ammonium or potassium fulminurate with silver nitrate. It is almost insoluble in cold water, but may be recrystallised from boiling water in long very thin needles. Heated with concentrated hydrochloric acid in sealed tubes, at 110°, traces of the oxides of carbon are produced; one-third of the nitrogen goes to form hydroxylamine hydrochloride, and the other two-thirds ammonium chloride (Ehrenberg). Under ordinary pressures at 100° the action is complicated.

The fulminurates of calcium, barium, strontium, iron, and lead may be obtained by double decomposition from ammonium or potassium fulminurates. On heating an ammoniacal solution of copper sulphate with fulminuric acid, dark-blue prisms of ammonium copper fulminurate are deposited on cooling. By passing hydrochloric acid gas through alcohol containing potassium fulminurate in suspension, Schischkoff obtained an oil which he considered to be ethyl fulminurate. This body is, however, not an ethyl salt of fulminuric acid, but has the composition $C_4H_6EtNO_5$. It readily forms additive compounds with ammonia and the amines (Ehrenberg, *l.c.*). According to Siedel (Ber. 1892, 2756), fulminuric acid forms two series of esters, the oxygen ethyl ester melting at 133° and the nitrogen ethyl ester at 155°.

Metafulminuric acid, *Isocyanuric acid* $C_3H_3N_3O_3$. It is obtained by the spontaneous polymerisation of fulminic acid (*q.v.*). It is best prepared by treating chloroformoxime with a small quantity of sodium hydroxide or with aqueous ammonia in the cold (Wieland and Hess, Ber. 1909, 1346). The hydrated acid, containing probably 2 molecules of water, melts at 85°–86°, and the anhydrous acid at 102°. On standing, metafulminuric acid changes into β-*iso*fulminuric acid. The constitution of metafulminuric acid is still under discussion. Wieland and Hesse (*l.c.*) consider the hydrated acid to be *iso*nitroso *iso*-oxazolone



whilst Palazzo and Tamburello (Chem. Zentr. 1907, i. 26) assign to it the constitution



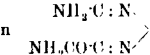
Cyan*iso*nitrosoacetohydroxamic acid, or oximinocyanoacetohydroxamic acid

$$C_3H_3O_3N_3+3H_2O, \text{ or}$$
$$HON:C(CN)\cdot C(OH):NOH$$

is obtained by warming metafulminuric acid with water. It is prepared by treating an ethereal solution of chloroformoxime with small quantities of ammonia, until the odour of the latter remains. The ammonium salt is decomposed with hydrochloric acid, and the acid, which crystallises from ether in colourless cubes, melts at 117°–118° (Nef, Annalen, 280, 324). *Cf.* Ulpiani (Gazz. chim. ital. 1916, 46, i. 1), who discusses the constitution of the fulminuric acids and describes a number of their derivatives.

*Iso***fulminuric acid** $C_3H_3N_3O_3$ of Ehrenberg is obtained by treating cyan*iso*nitrosoacetohydroxamic acid with ammonia. It is a powder, and chars without melting when heating (Nef, *l.c.*; Ehrenberg, J. pr. Chem. [2] 30, 55).

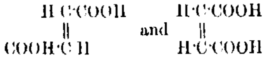
β-*Iso***fulminuric acid** was obtained by Scholvoin (*ibid.* [ii.] 32, 461). He treated sodium fulminate with dilute sulphuric acid, and allowed the metafulminuric acid thus formed to stand for some time. Ulpiani (Gazz. chim. ital. 1905, iii. 35, 7) obtained the amide of this acid by treating succinamidedinitrosoperoxide with concentrated ammonia. The amide has the constitution



$$\begin{matrix} NH_2\cdot C:N \\ \qquad\qquad >O \\ NH_2CO\cdot C:N \end{matrix}$$

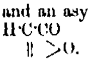
, and the acid is obtained from it by hydrolysis. When anhydrous, the acid melts at 196° with decomposition; the hydrated acid melts at 188°.

FUMARIC ACID and MALEIC ACID



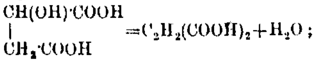
$$\begin{matrix} H\cdot C\cdot COOH \\ \| \\ COOH\cdot C\cdot H \end{matrix} \quad \text{and} \quad \begin{matrix} H\cdot C\cdot COOH \\ \| \\ H\cdot C\cdot COOH \end{matrix}$$

These two unsaturated acids are regarded as stereoisomers, and because of the readiness with which maleic acid forms an anhydride, maleic acid is represented as the *cis*- modification, and fumaric, which forms no anhydride, as the *trans*-modification. Interesting confirmation of this is shown by the formation of maleic acid on oxidising benzoquinone with nascent silver peroxide (Kempff, Ber. 1906, 3715). Maleic acid chloride is a very reactive compound, and an asymmetric structure is attributed to it,



$$\begin{matrix} H\cdot C\cdot CO \\ \| \quad >O \\ HC\cdot CCl_2 \end{matrix}$$

. The chloride of furmaric acid is much less reactive (Ott, Ann. 392, 245). These two unsaturated dibasic acids may be obtained by heating malic acid:



$$\begin{matrix} CH(OH)\cdot COOH \\ | \\ CH_2\cdot COOH \end{matrix} = C_2H_2(COOH)_2 + H_2O\,;$$

maleic anhydride $C_4H_2O_3$ distils over, and fumaric acid remains behind in the retort. By rapid distillation at 110°–140°, maleic anhydride is obtained as chief product; by heating for about 40 hours to 150°, fumaric acid is mainly formed.

Both acids when treated with nascent hydrogen yield succinic acid. Both unite with hydrobromic acid to form monobromosuccinic acid. But fumaric acid unites with bromine to form dibromosuccinic acid, whilst maleic acid gives *iso*dibromosuccinic acid. Potassium permanganate oxidises fumaric acid to racemic acid; maleic acid is converted into mesotartaric acid. Fumaric acid is much less soluble in water than maleic acid.

Fumaric acid occurs in various plants, as in the common fumitory (*Fumaria officinalis* [Linn.]), in *Corydalis bulbosa*, *Glaucium flavum* (Crantz), *Cetraria islandica* (Ach.), Euphorbiaceæ Clytia similis, and in varieties of *Agaricus*. It is also formed during the growth of *Rhizopus nigricans* in dextrose-containing media. It occurs in fresh beef, as an oxidation product of succinic acid (Zeitsch. physiol. Chem. 90, 301). It can be prepared by heating halogen substituted succinic acids (Brunner and Chuard, Ber. 1897, 201; Swarts, Zeitsch. Chem. 1868, 25); by reduction of tartaric acid (D. R. P. 254, 420); by condensing malonic with glyoxylic acid in presence of pyridine; and from maleic acid (*v. infra*). When heated in a sealed tube it melts at 286°–287° (Michael, Ber. 1895, 163); sp.gr. 1·625 (Tanatar, Chem. Soc. Abstr. 1893, i. 11). It crystallises in small prisms, which sublime at 200° without decomposition, but by distillation is converted into maleic anhydride and water. Fumaric acid forms no anhydride of its own; all processes of dehydration convert it into maleic anhydride, which unites with water to form maleic acid.

Fumaric acid is converted into maleic acid by ultra-violet light, and also under the influence of radium rays. Fumaric acid on heating in aqueous solution is converted to malic acid, the change being a reversible one (James and Jones, Trans. Chem. Soc. 1912, 1158).

Maleic acid has never been found to occur in nature, and is best obtained by heating malic acid with acetyl chloride, and decomposing the acetyl maleic anhydride into maleic anhydride and acetyl chloride, and then heating the anhydride with water. It can also be prepared by heating fumaric acid (*v. supra*), or by treating a mixture of the vapours of benzene and benzoquinone by oxygen under pressure in presence of vanadium oxide (Weiss and Downs, U.S. Pat. 1318632). It forms large prisms or tabular crystals, very soluble even in cold water, m.p. 130°, b.p. 160°, decomposing for the most part into anhydride and water. Maleic acid is converted into fumaric acid when it is heated for some time at 130° or in sealed tubes at 200°, when it is treated in the cold with dilute mineral acids and certain organic acids, with sulphuretted hydrogen followed by sulphur dioxide, or with bromine in sunlight. Even at ordinary temperatures, and in the dark, its aqueous solution is slowly converted into fumaric acid. By heating the esters of maleic acid with iodine, the esters of fumaric acid are produced.

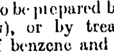
Maleic anhydride is a white crystalline solid, melting at 56° and boiling at 196°.

FUMARINE. Protopone (*q.v.*).

FUNGICIDES *v.* DISINFECTANTS and PLANT-SPRAYS.

FUNGISTEROL *v.* ERGOT.

FURFURAL, *Furfurol, Furfuraldehyde, Pyromucic aldehyde* $C_5H_4O_2$,



$$\begin{matrix} CH{=}CH \\ | \qquad\quad >O \\ CH{=}C\cdot CHO \end{matrix}$$

first obtained by Döberciner by distilling sugar with manganese dioxide and dilute sulphuric acid. It may be prepared in small yields by heating sugar with dilute tartaric or lactic acids, or simply by heating with water; hence it occurs in brewers' wort and sometimes in the finished beer, also forming a constituent of fusel oil from the distilleries. Is produced during the heating of madder with dilute sulphuric acid in the preparation of garancin; during the dry distillation of oak timber; and by heating starch at 200°. It is a constituent of many essential oils (Schimmel). Best prepared by distilling bran with dilute sulphuric acid and fractionating the distillate.

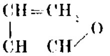
Colourless liquid; b.p. 161°; smelling of oil of bitter almonds and oil of cinnamon; sp.gr. 1·1594 at 20°/4°; $\mu a = 1{\cdot}5186$; soluble in 11 parts of water at 13°.

Reduces silver oxide with formation of pyromucic acid. Shows a striking similarity to benzaldehyde in its reactions, forming furfur-alcohol and pyromucic acid with caustic potash, furfoïn with potassium cyanide, dyestuffs with derivatives of aniline, &c.

The *urethane* is a very characteristic derivative, crystallising in needles, m.p. 169°, which may be sublimed. The *semicarbazone* melts at 202°–203°.

Owing to the presence of furfural in beer and spirits, many methods have been devised for its detection. One of the most sensitive tests is with colourless aniline, absolute alcohol, and either hydrochloric or glacial acetic acid, a cherry-red coloration being produced, the amount of furfural present being estimated by the depth of colour (J. Amer. Chem. Soc. 1906, 1629). Other methods of estimation are: precipitation with phloroglucin and hydrochloric acid (Weibel and Zeisel), and the preparation of the insoluble semioxamazide.

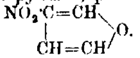
FURFURAN, *Furan, Tetrol, Tetraphenol*



Is a fairly stable ether compound, obtained by the distillation of the barium salt of pyromucic acid with soda-lime; by the distillation of calcium succinate; or by heating succinic dialdehyde with water at 180°. Best prepared by heating pyromucic acid alone in a tube at 260°–275°, as the barium salt produces also the hydrocarbon C_3H_4 and CO (Freundler, Compt. rend. 124, 1157).

Appears to be contained in the volatile portions of pinewood tar. Colourless liquid, boiling at 32°; insoluble in water, readily soluble in alcohol and ether. Acids convert it into pyrrole-red; metallic sodium and alkalis do not attack it. Colours a chip of pinewood moistened with hydrochloric acid an emerald green.

By nitration in presence of acetic anhydride, a monoacetin of nitrosuccinicaldehyde is formed, which reacts with pyridine, producing nitrofurfuran; m.p. 28°;



FURFURINE $C_{15}H_{12}N_2O_3$. Prepared from furfural by first making the amide with the aid of ammonia. Furfuramide is boiled for 15 minutes with very dilute caustic potash, and the furfurine which separates is dissolved in excess of boiling dilute oxalic acid. The so-formed dioxalate is collected, and again dissolved in 100 parts boiling water, and precipitated with ammonia (Bahrmann, J. pr. Chem. [2] 27, 313); white needles; m.p. 116°; very sparingly soluble in cold water, but appreciably soluble in hot; readily soluble in alcohol or ether. It is a mono-acid base, and the crystals turn brown in moist air. Expels ammonia from boiling solutions of ammonium salts, but is itself precipitated by ammonia from its salts in the cold.

When heated with sodium, *iso*furfurine is formed. Forms a nitrosamine $C_{15}H_{11}(NO)N_2O_3$ by acting on the sulphate with very dilute potassium nitrite, and this exists as golden triclinic crystals; m.p. 112° (Schiff, Ber. 11, 1250).

FURFUROIDS are a group of compounds closely related to the pentoses and pentosans, distinguished by yielding furfural as a characteristic product of decomposition on treatment with acids (Cross, Bevan, and Smith, Chem. Soc. Trans. 1897, 1001).

FURFUROL *v.* FURFURAL.

FURNACES FOR GENERAL LABORATORY USE. Fig. 1 shows a Fletcher's gas muffle furnace affording high temperatures without an air blast. With the use of a suitable pressure governor, fairly constant temperatures may be obtained. The furnace can be used for heating precipitates, fusions, roasting of ores, and similar laboratory operations. When crucibles which have to be weighed are heated, a sheet of asbestos cloth should be placed on the floor of the muffle.

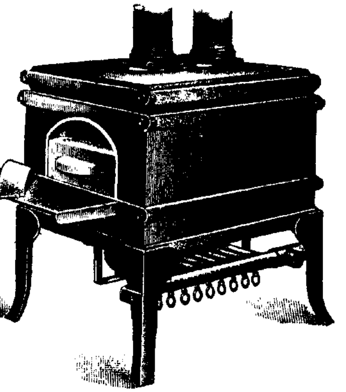


Fig. 1.

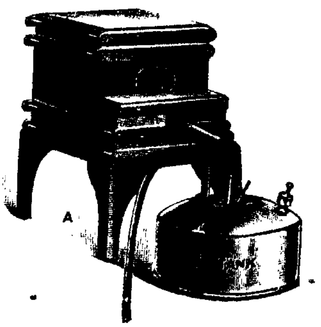


Fig. 2.

A Fletcher's muffle furnace (Fig. 2), in which petroleum is used as fuel, is designed for use where gas is not available. With the burner shown, the necessary air-blast may be obtained by a foot blower; or an automatic petroleum burner may be used, which dispenses with the use of an external supply of compressed air.

Fig. 3 shows a Fletcher's injector furnace, which is efficient and rapid in working. For ordinary purposes, a foot blower is used, but for very high temperatures a blower driven by power is preferable. Cast iron can readily be fused in this furnace.

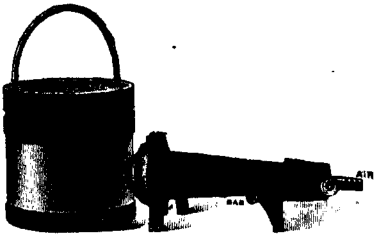


FIG. 3.

A furnace of similar shape to that shown in Fig. 3, but with a modified burner, is used where extremely high temperatures are required, a stream of oxygen being employed instead of the usual air blast. In order to prevent the perforation of crucibles by a small but extremely hot flame, the burner is so designed that the oxygen is mixed with air before it enters the furnace, a more diffused flame being thus obtained.

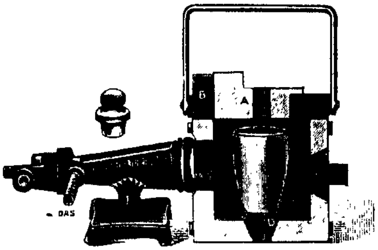


FIG. 4 (*a*).

An exceedingly useful furnace designed by Fletcher is shown in Fig. 4 (*a* and *b*). This furnace works either as a draught or blast furnace with the same burner, and may be used for any temperature up to the fusing-point of the casing. It is adapted for crucibles, muffles, tubes, cupels, distillation by descension, treatment of refractory substances with gases at high temperatures, small forgings, roasting of ores, &c. When used as a blast furnace as shown in the figure, an empty crucible can be raised to the fusing-point of cast iron in 2 minutes, starting all cold. For use as a draught furnace, the plug C is removed and replaced by a chimney, when a crucible may be heated to bright redness in 10 minutes. The furnace may also be turned on its side, when the doors A and B become the front of a muffle furnace.

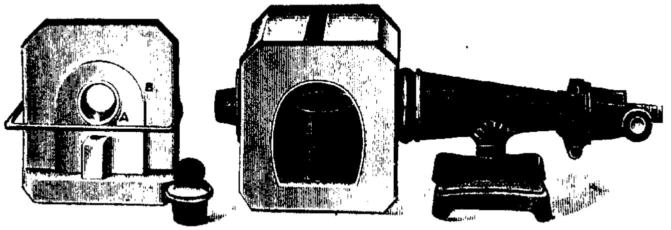


FIG. 4 (*b*).

A furnace in which magnesia is used as the refractory material, and designed to employ the oxygen-coal gas flame is made by Merck. The burner is provided with a water jacket; and the mixed gases, which are projected through the bottom of the furnace, are so directed that the flame does not play directly on the substance in the crucible. The employment of magnesia for the parts most exposed to the flame, admits of the use of a very high temperature.

Fig. 5 shows a Fletcher's reverberatory furnace available for all general laboratory work, and capable, when working with a draught, of producing a clear yellow heat above the fusing-point of fine silver, and when worked with a blast, for which the same burner is employed, of melting cast steel. It may be employed as shown, or one or both doors may be arranged to receive a muffle, so that the furnace may be used for muffle or crucible operations, or for both simultaneously. Perrot's furnace for heating crucibles by gas is described fully in Bull. Soc. chim. 1867, 7, 332.

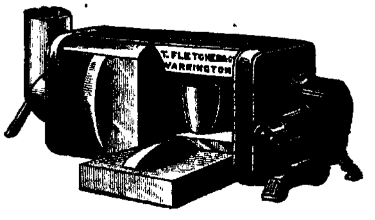


FIG. 5.

A furnace designed by Rössler (Zeitsch. anal. Chem. 1886, 95; Dingl. poly. J. 253, 79; J. Soc. Chem. Ind. 1884, 512) for intensely heating small crucibles employed in chemical analysis is shown in Fig. 6. Cold air, admitted in carefully regulated quantity at *e* to the burner *a*, becomes heated during its passage around a jacket, *d*. Combustion takes place within a muffle, *c*, surrounding the crucible *b*, and the combustion products pass out through the cover of the muffle and through a chimney, *g*, the draught in which is assisted and regulated by a second burner. A somewhat similar arrangement has been described by Hempel (Zeitsch. anal. Chem. 1877, 454). A simple form of crucible furnace using gas has been described by Roberts and McDermott (J. Amer. Chem. Soc. 1911, 33, 507).

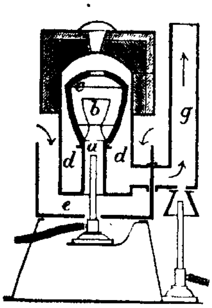


FIG. 6.

Fig. 7 shows a Fletcher's furnace, which, although primarily designed for organic analysis, will be found very useful for many other laboratory operations. The burners are placed in front of the furnace, and clear from all falling dirt, and since these are made of brass, there is no ironwork to rust. The furnace is made in 6-inch sections, and can, therefore, be built up to any length. The body of the furnace is made entirely of fire-clay.

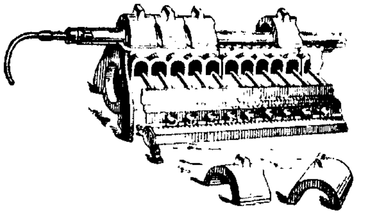


FIG. 7.

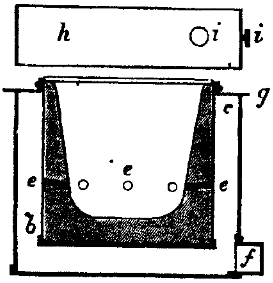


FIG. 8.

Sefström's portable furnace for use with charcoal is shown in Fig. 8. It consists of an outer cylinder forming an air chamber around a cylinder, *b*, fixed in position by a flange, *g*. The cylinder *b* is perforated with holes containing small tapering nozzles, *e*, and is lined with fire-clay shaped as shown. When greater space is required for fuel, &c., a hoop, *h*, may be placed around the top of the cylinder *b*. It consists of a strip of sheet iron, in one end of which are two holes, *i*, whilst in the other end is a button which may be inserted in either of the holes, so that the hoop may fit over the cylinder *b*, or, when not in use, over the outer cylinder. The blast is supplied at *f* by a small bellows.

The electric furnace shown in Fig. 9 is specially adapted for fusions on a small scale, and for the production of high local temperatures. The process can be watched from beginning to end through the mica doors, the eyes being protected by blue spectacles. The furnace consists of an iron muffle lined with fire-clay. The block *b* can be raised or lowered by means of the set-screw *c*. On this block stands the crucible, made of lime, magnesite, &c., according to the purpose required. The cables *f* and *f′* convey the current to the electrodes, *a* and *a′*, which can be adjusted by means of the regulating wheels *e* and *e′*. The mica doors permit of easy access to the interior of the furnace. In this type of furnace the heat is generated in a chamber of practically non-conducting material, and since no cold gases are introduced, extremely high temperatures may be produced in the crucible.

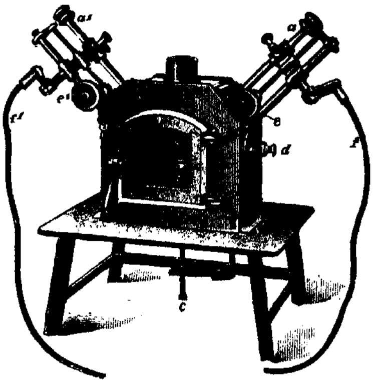


FIG. 9.

In the tube furnace shown in Fig. 10, the heating body consists of a tube of highly refractory porcelain, around which is coiled a ribbon of very thin platinum, which makes a closer contact with the porcelain and lasts much longer than platinum wire. A temperature of 1400° can easily be reached, but above this the porcelain begins to conduct electricity, and an electrolytic action is set up between the platinum and the tube, which will eventually cause breakage. In the figure the furnace is shown mounted on a tilting frame for use in any position. It may be obtained wound for any supply between 65 and 250 volts. In using the furnace it is necessary to pay attention to the following points: (1) No cold object must be brought into contact with the tube while it is incandescent. (2) The furnace should not be kept at its maximum temperature longer than is necessary. (3) A suitable resistance should be connected up with the furnace in order to ensure gradual heating, and to provide a means of regulating the temperature.

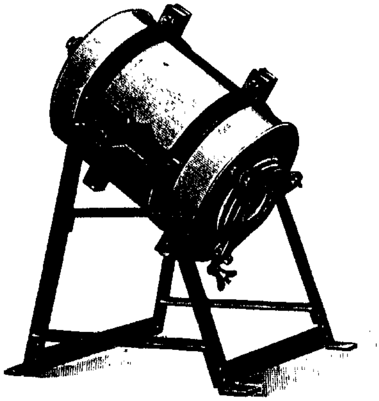


Fig. 10.

Fig. 11 shows an electrically heated crucible furnace, in which the heating resistance consists of platinum wire embedded in a suitable fireclay. The furnace is designed for crucibles of a capacity not exceeding 30 c.c., and the temperature obtained is about 1050°-1100°. Inside the furnace the crucible rests upon a small stand of refractory porcelain; but if the contents of the crucible are moist, and it is required to heat them slowly, the crucible is suspended in such a way that only the lower part is within the furnace. For quantitative work, the furnace cover can be coated with platinum foil in order to prevent chips of fireclay from falling into the crucible, and in special cases the whole of the interior may be so lined. The temperature obtained is more uniform than that produced by the gas blowpipe, and the use of this furnace entirely prevents the damage, which, particularly in the analysis of phosphates, is caused by the reducing gases, to a platinum crucible heated by gas. The consumption of current at 110 volts is 2·3 ampères, and the platinum resistance has an average life of about 850 burning hours.

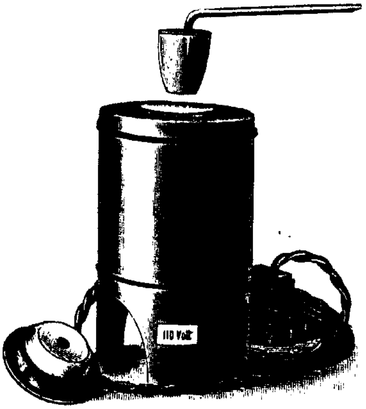


Fig. 11.

An electrical crucible furnace in which the platinum resistance is replaced by a common metal is described by Askenasy (Zeitsch. Elektrochem. 1914, 20, 253). The metal is prevented from oxidising by a packing of powdered charcoal, which is placed in the space between the actual furnace and the outer casing. The furnace is 50 mm. diameter and 80 mm. deep, and can be connected directly with the lighting circuit without any resistance in series. The efficiency of the furnace is high, and a temperature of 800° can be obtained in 10 minutes, and one of 1100° in 30 minutes.

A crucible furnace in which the heat is generated by the passage of an electric current through a resistance of granular carbon, is made by Merck (Fig. 12). In order to withstand very high temperatures, the parts most exposed to the heat are made of magnesia, which is also used as a packing to minimise loss of heat. When using the maximum amount of energy (about 8000 watts), the temperature approaches the melting-point of corundum.

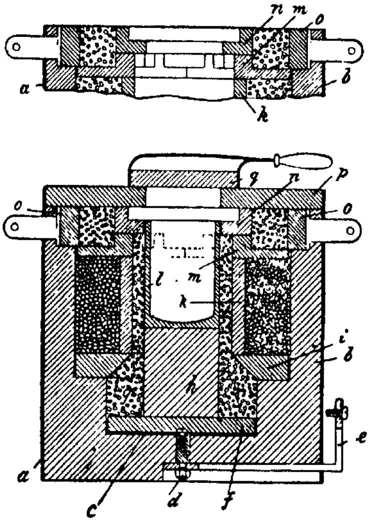


Fig. 12.

a, *b*, Case; *c*, copper plate; *d*, bolt; *e*, terminal; *f*, carbon block; *g*, resistance; *h*, crucible stand; *i*, magnesite ring; *l*, heating chamber; *m*, *n*, rings of magnesia; *o*, annular electrode; *p*, large cover; *q*, small cover.

An electrically heated tube furnace (Fig. 13) is described by Blount (Analyst, 1905, 30, 29), in which the resistance consists of loosely packed retort carbon mixed with a suitable quantity of siloxicon. The essential parts of this furnace are two concentric fire-clay tubes, surrounding, but not actually touching, that part of the porcelain tube to be heated. The resistance material is packed between these two fire-clay tubes, the current being led in by means of an annular copper disc at each end, which is provided with a short cylindrical projection fitting closely in between the two tubes so as to make good contact for the resistance material. The two tubes which form the furnace proper are surrounded by two other wider fire-clay tubes which serve merely to insulate the heat. They may be covered with asbestos wrapping still further to retain the heat. The ends of the furnace are made of uralite discs, which also support the tube to be heated. With this apparatus, a piece of copper weighing from 15 to 20 grams can be fused in about 18 minutes.

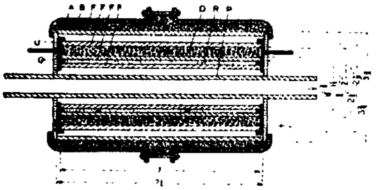


FIG. 13.

A, clamps; B, asbestos cloth; C, copper terminals; F, fire-clay tubes; D, pieces of fire-clay, R, resistance mixture; P, porcelain tube; U, uralite discs.

A simple electric laboratory furnace with resistor of ductile tungsten or molybdenum wound on an alundum cylinder has been described by Winne and Dantsizen (Met. & Chem. Eng. 1911, 9, 537; J. Soc. Chem. Ind. 1911, 30, 1264). The temperature can be raised to 1700°, at which a current of 25 volts and 45 ampères is required.

For temperatures up to 2100°, electrically heated furnaces are made in which a current of 500 ampères and 5 volts is led through a thin-walled tube of pure iridium, but the extremely high price of this metal greatly limits the use of these furnaces.

For other forms of electric furnaces, *see* Pring, The Electric Furnace, Longmans, 1921.

For descriptions of electric vacuum furnaces, *see* Goecke, Metallurgie, 1911, 8, 667; *also* Slade, Proc. Roy. Soc. 1912, A. 87, 519; Wolf and Müller, Zeitsch. Elektrochem. 1914, 20, 1; Ruff, *ibid.* 1914, 20, 177; Oesterheld, *ibid.* 1915, 21–54.

Furnaces employed for particular purposes will be found described under special headings, as ASSAYING; ALUMINIUM; &c., &c.

FURUNCULINE *v.* SYNTHETIC DRUGS.

FUSEL OIL. *Fermentation amyl alcohol, Potato oil, Grain oil, Marc brandy oil.* (Ger. *Fuselöl*; Fr. *Huile de pommes de terre.*) The mixture of alcohols constituting this substance is produced in comparatively small quantity in the alcoholic fermentation of most bodies containing sugar, the largest proportion being contained in the alcohol prepared from potatoes, while in the alcohol from the 'marc' of grapes and from beetroots, grain, &c., smaller quantities are found.

Fusel oil consists mainly of two alcohols, one of which, *iso*-butyl carbinol, or *iso*-amyl alcohol, or inactive amyl alcohol $(CH_3)_2CH{\cdot}CH_2CH_2{\cdot}OH$, is optically inactive, while the other, secondary butyl carbinol or active amyl alcohol

$$C_2H_5{\cdot}CH_3{\cdot}CH{\cdot}CH_2{\cdot}OH,$$

rotates the plane of polarised light to the left sufficiently to render fusel oil strongly lævorotatory. The following alcohols are said to have been separated from fusel oil:—

Ethyl alcohol . .	$CH_3{\cdot}CH_2{\cdot}OH$.
Normal propyl alcohol	$C_2H_5{\cdot}CH_2{\cdot}OH$.
*iso*Propyl „	$(CH_3)_2CH{\cdot}OH$.
Normal butyl „	$C_3H_7{\cdot}CH_2{\cdot}OH$.
*iso*Butyl „	$(CH_3)_2CH{\cdot}CH_2{\cdot}OH$.
Tertiary butyl „	$(CH_3)_3C{\cdot}OH$.
Active amyl „	$C_2H_5(CH_3)CH{\cdot}CH_2{\cdot}OH$.
Inactive amyl „	$(CH_3)_2CH{\cdot}CH_2{\cdot}CH_2{\cdot}OH$.
Methyl normal propyl carbinol . .	$CH_3(C_3H_7)CH{\cdot}OH$.
Normal primary amyl alcohol . .	$C_5H_{11}{\cdot}OH$.
A primary hexyl alcohol	$C_6H_{13}{\cdot}OH$.
„ heptyl „	$C_7H_{15}{\cdot}OH$.

Formic, acetic, propionic, butyric, valeric, caproic, œnanthic, caprylic, pelargonic, and capric acids have been found in fusel oils, and ethyl acetate and other esters and various aldehydes are also present.

The composition of fusel oil depends on the source of production, the nature of the ferments (*vide infra*), and the method of distillation. That from grain or potatoes consists largely of amyl alcohols with ethyl alcohol, the inactive amyl alcohol being the principal constituent. The fusel oil prepared in the South of France from the marc of brandy contains normal propyl alcohol in considerable quantities, while that obtained from the beet contains a larger proportion of *iso*butyl alcohol. Also the ferment in brewer's yeast (*Saccharomyces cerevisiæ* [Meyer]) appears to favour the production of *iso*butyl alcohol, whilst *Saccharomyces ellipsoides* (Reess.) (from the grape) tends to produce normal butyl alcohol. Higher alcohols are said to be rapidly produced after fermentation ceases, and, therefore, the higher alcohols tend to increase the longer the interval between fermentation and distillation. This may be due to some organism other than yeast becoming active after the yeast has done its work.

The proportion of fusel oil obtained during fermentation is also modified by the condition of the mash. Alkaline liquids, particularly when warm and containing large quantities of sugar, promote its formation, while acid liquids, especially when containing tartaric, racemic, or citric acids, are said to prevent its production. The presence, in any quantity, of tartar or certain bitters such as that of hops also prevents its formation, so that wines, &c., are usually free from fusel oil. According to Le Bel (Compt. rend. 96, 1368), pure sugar fermented with beer yeast yields less of these alcohols than wine or beer. Obviously a larger proportion of higher alcohols is likely to occur in spirits distilled from a pot-still than when highly rectifying appliances are used, as in patent stills.

Fusel oil is contained principally in the alcoholic distillates commencing to come off at 105°–125° and ending at 132°–137°. Between 105° and 120° most of the *iso*butyl alcohol is obtained, while the amyl alcohols distil principally between 128° and 132°.

According to Rabuteau (Compt. rend. 87, 500), the following represents the percentage by volume of the principal constituents of *potato oil* :—

*iso*Propyl alcohol . . .	15·0
Propyl ,, . . .	3·0
Normal butyl alcohol . .	6·5
*iso*Butyl ,, . . .	5·0
Inactive amyl ,, . .	27·5
Active ,, ,, . .	6·0
Products boiling above 132° and retaining amyl alcohol . .	17·0
Ethyl alcohol, ethyl acetate, and aldehyde	7·5
Water	12·5
	100·0

Later observations, however, do not confirm Rabuteau's statement that fusel oil contains *iso*propyl alcohol.

According to Ulex, the distillation of fusel oil produced from (1) beet, (2) potatoes, (3) grain, gives (roughly) the following percentage by volume :—

	(1)	(2)	(3)
80°–100° (principally propyl alcohol)	13	13	31
100°–130° (butyl and amyl alcohols)	53	30	26
Above 130° (amyl alcohol) .	34	57	43

By careful fractional distillation of wine brandy 25 years old, Ordonneau (Compt. rend. 1886, 102, 217) obtained the following substances :—

	P.c. by volume
Aldehyde	0·003
Ethyl acetate . . .	0·035
Acetal	traces
Œnanthylic ester . . about	0·004
Propionic, butyric, and caproic esters	0·003
Normal propyl alcohol . .	0·040
,, butyl ,, . .	0·218
'Amyl alcohol' . . .	0·0838
Hexyl ,, . . .	0·0006
Heptyl ,, . . .	0·0015
Amine bases (probably of the pyridine series) . . .	traces

Commercial alcohols from maize, beet, and potatoes, showed the presence, in addition to other substances, of propyl alcohol, active and inactive amyl alcohol, pyridine, a base which appeared to be collidine, and *iso*butyl alcohol, without a trace of normal butyl alcohol. Ordonneau attributes the disagreeable difference in flavour between wine brandy and that from a mash to the presence in the former of normal butyl alcohol, while the latter contains the disagreeably smelling *iso*butyl alcohol, but no normal butyl alcohol. He recommends that the fermentation of a mash should be performed with the elliptic *wine* yeast instead of the globular *beer* yeast, as he finds by experiment that the former produces the normal butyl alcohol, while the latter tends to form the *iso*- variety.

The *iso*-amyl alcohol (inactive amyl alcohol) may be separated from fusel oil by agitation with a saturated solution of common salt. The amyl, butyl, and propyl alcohols, which are less soluble in that medium than in water, separate as an oily layer, while the ethyl alcohol remains in the brine. The separated oil is distilled, the portion coming off between 105° and 120° consisting principally of *iso*-butyl alcohol, while that distilling between 125° and 140° contains the amyl alcohols. This is collected separately, agitated with hot milk of lime, dried over calcium chloride and redistilled, the portion coming off between 128° and 132° being collected separately. In this way the *iso*-amyl alcohol is obtained almost free from butyl alcohol and from valeric aldehyde. The barium amyl sulphate produced from active amyl alcohol is 2½ times as soluble in water as that from the inactive variety, so that these salts may be separated by careful fractional crystallisation, and afterwards treated for reproduction of the alcohols.

The composition of fusel oil from various sources has been carefully studied by Karl Windisch (*v.* Arbeiten aus dem Kaiserlichen Gesundheitsamt, 1892, Bd. 8), his principal results from (1) potato and (2) corn fusel oil, expressed in grams per kilog., and excluding ethyl alcohol and water, being as follows :—

	(1)	(2)
Normal propyl alcohol	68·54	36·90
*iso*Butyl alcohol .	242·50	157·60
Amyl ,, .	687·60	758·50
Hexyl ,, .	—	1·33
Heptyl ,, .	—	trace
Free fatty acids .	0·11	1·60
Fatty acid esters .	0·20	3·05
Furfural and bases .	0·05	0·21
Terpenes . .	—	0·33
Terpene hydrate .	—	0·48

The free fatty acids and acid esters were also analysed with the following results expressed in percentages, the acids and esters being taken together in the potato fusel oil, and separately in the fusel oil from corn :—

	Potato.	Corn	
	Free fatty acids and acids esters	Free fatty acids	Esters
Capric . .	36	44·1	40·7
Pelargonic .	12	12·9	14·2
Caprylic .	32	26·7	34·8
Caproic .	14	13·2	9·6
Butyric . .	0·5	0·4	0·4
Acetic . .	3·5	2·7	0·3

The terpene $C_{10}H_{16}$, which is present, together with its hydrate $C_{10}H_{18}O$, has not been exactly identified, but it has a close resemblance to phellandrene.

The injurious effect of raw or recently manufactured spirits is attributed (*inter alia*) to the presence of fusel oil produced during the fermentation and not thoroughly separated. Bell considered it to be due rather to furfural and other empyreumatic bodies, and this view was supported by Lauder Brunton, who thought that the toxic effect of spirit may also be attributed, in some cases, to the presence of traces of alkaloidal bodies, arising from the decomposition of albuminous substances in the mash. Schidrowitz also found in new whisky substances such as pyrrol, phenolic bodies, traces of nitriles, &c., which disappear as the spirit matures (J. Soc. Chem. Ind. June, 1905). The actual adulteration of alcoholic liquors with fusel oil is improbable, but spirits containing 0·3 p.c. of that substance are usually deemed to be injurious, although the general tendency of the evidence given before the Royal Commission on Whisky and Potable Spirits, was to show that the evil effect of spirits is due to the ethyl alcohol itself, rather than to fusel oil or other secondary products present.

Samples of spirits examined by Dupré (Analyst, 1, 6) contained for 100 parts by weight of ethyl alcohol :

Scotch whisky containing 54·5 p.c. of alcohol	0·9	p.c. amyl alcohol
Cape smoke . .	0·24	,,
Common Samshoe .	0·18	,,
Fine ,, .	0·13	,,

According to Le Bel (Compt. rend. 96, 1368), natural white wine contains 0·2 p.c. amyl alcohol per litre, and, according to Hamberg (Schmidt's Jahrb. der Medicin, 201, 27, 1885), beer contains about 0·00114 p.c. of fusel oil.

Beer recommends a maximum permissible limit to the fusel oil in brandy, liqueurs, &c., of 0·3 p.c. ; but Bödlander and Traube (Rep. Anal. Chem. 7, 167), who have examined a number of commercial spirits, propose a limit of 0·10–0·15 p.c.

The separation of fusel oil from spirit is extremely difficult. Among the various substances proposed or used for its destruction or removal, are charcoal, soap, oil, and fatty substances, potash (' grey salts '), pearl ash (' white salts '), lime, sulphuric, nitric, and hydrochloric acids, bleaching powder, and potassium permanganate.

Charcoal, soap, and oil are supposed to separate the fusel oil unchanged. When rectified over potassium permanganate or bleaching powder, the amyl alcohols are converted into valerates, but a portion of the ethyl alcohol is also decomposed. Bleaching powder, when used, is made into a milk at the ordinary temperature and permitted to digest for a time, after which the spirit is drawn off and rectified. According to Klozensky, if the spirit be distilled from *hard soda soap*, the fusel oil remains with the soap, from which it may be separated by subsequent distillation at a more elevated temperature.

The most approved method of separation, however, is by well-burnt granulated vegetable charcoal or bone-black. The charcoal is placed upon perforated trays in a vessel surrounded by a cooling jacket, and the spirit, usually diluted to about 160°Tr., is caused to pass through several layers. The operation should not be performed above the ordinary temperature, as the fusel oil is again dissolved from the charcoal near the boiling temperature. From 3 to 5 vols. of charcoal are required for the successful treatment of 100 vols. of brandy. The whole of the fusel oil is evolved from the charcoal on treatment by superheated steam, and the charcoal may be repeatedly used after heating to redness to drive off the occluded gases, &c. It is noticeable that the fusel oil obtained by steaming the charcoal does not represent the whole of that removed from the spirit, nor are sufficient compounds which might be produced by the decomposition of the fusel oils found to account for this loss.

Raw brandy, produced in Switzerland from potatoes, maize, and the residues from breweries, by the continuous process, has been found to contain 1·32 p.c. of fusel oil. Raw Swiss brandy filtered through charcoal showed 0·2 p.c. of fusel oil ; that rectified by distillation, 0·06 ; and that filtered through charcoal and afterwards rectified contained none. *Cf.* F. Pampe (Chem. Zeit. 11, 313).

Apart from the desirability of removing the excess of fusel oil from spirits intended for human consumption as a beverage, the oil is recovered for its own sake, as a valuable by-product in the manufacture of spirit, its price before the war being about 6 times that of ordinary alcohol. During the war, owing to the great demand for fusel oil for the manufacture of amyl acetate and other purposes, the price increased fourfold, viz. from about 50*l.* to over 200*l.* per ton.

By means of patent stills, the fusel oil may be rapidly and almost completely removed, and with suitable rectifying apparatus, alcohol at 95° and fusel oil may separately be obtained in the proportions of 130 to 1, or nearly 0·8 p.c. (by volume) of fusel oil.

The amyl alcohols of fusel oil dissolve in about 40 parts of cold water. According to Balbiano (Ber. 9, 1437), the inactive variety is soluble in about 50 parts of water at 14°, and is less soluble at 50°. *Iso*butyl alcohol dissolves in 10 parts of water at 15°. One part of inactive amyl alcohol takes up about 0·08 part of water, while *iso*butyl alcohol dissolves nearly twice that amount.

Fusel oil dissolves freely in ether, chloroform, alcohol, benzene, and carbon tetrachloride.

It is largely used for the manufacture of amyl acetate (*v.* ACETIC ACID), which has numerous applications in the arts and manufactures, as flavouring essences (pear oil, &c.), for confectionery, as a solvent for cellulose, and in making lacquers, varnishes, artificial leather, waterproofing, and sanitary sheeting for hospitals, &c. It is also used in toxicology as a solvent for alkaloids, for which purpose it should be carefully purified by agitation with dilute acid to remove an alkaloidal body which it is liable to contain. On account of its strong affinity for chlorine, fusel oil has been employed in chlorine generators for laboratory purposes as an absorbent for that gas, to prevent its escape into the atmosphere when the supply is no longer required ; whilst its principal constituent (amyl alcohol) is employed in the estimation of fat in milk by the centrifugal methods.

For a description of the method of valuation of fusel oil used in the Institut für Gärungsgewerbe, Berlin, *see* Heinzelmann, Z. Spiritusind. 1912, 35, 612 ; J. Soc. Chem. Ind. 1912, 31, 1142.

Synthetic fusel oil.—Synthetic commercial amyl acetate and fusel oil can be prepared by the following operations : A gasoline, boiling at 25°–45°, and consisting chiefly of saturated hydrocarbons, as, for instance, that obtained by cooling natural gas, is chlorinated by introducing chlorine at one end of a body of the hydrocarbon whilst illuminating the other end with a source of actinic light, and causing the gas to approach the light. By this means monochloro- derivatives are obtained, and as soon as these have accumulated to the extent of 20 p.c. the mixture is fractionated, and the unchanged hydrocarbons are recovered for retreatment. The fraction, b.p. 95°–140°, consisting mainly of pentyl and hexyl chlorides, is heated with an equal weight of anhydrous sodium acetate (with or without acetic and amyl acetate) for 5 hours at 200° under pressure in an autoclave rotated 30 times per minute. In this way 580 lbs. of the crude chlorides gave 384 lbs. of crude amyl acetate, from which fusel oil may be obtained by hydrolysis (Essex, Hibbert, and Brooks, J. Amer. Chem. Soc. 1916, 38, 1368). Another method consists in heating the chlorides with methyl alcohol and a formate under pressure at 140°–190° (Brooks and Essex, U.S. Pat. 1221667, 1917; Pyman, Reports, &c., 1917, ii. 471).

Detection of fusel oils.—When a sample of spirit is poured on filter paper or on the hand, and allowed to evaporate spontaneously, the characteristic suffocating odour of fusel oil may be recognised towards the close of the evaporation. So small a quantity as $\frac{1}{2000}$ part of amyl alcohol in gin may thus be detected.

On dissolving 1 gram of caustic potash in 150 c.c. of the spirit, concentrating slowly to 15 c.c., and adding an equal volume of dilute sulphuric acid, a powerful odour is given off, which is frequently sufficiently distinctive to show the nature of the mash from which the spirit was obtained. Betali (Ber. 8, 72) adds to the alcohol 6–7 volumes of water, and agitates with sufficient chloroform to produce a small layer on subsidence. This layer is drawn off and evaporated, and the residue is tested by digestion with potassium acetate and sulphuric acid. In presence of fusel oil the characteristic pear-like odour of amyl acetate is observable.

Marquardt dilutes 40 c.c. of the spirit with sufficient water to raise the density to about 0·980, and agitates the mixture with 15 c.c. of pure chloroform, which, after settlement, is drawn off, shaken with an equal volume of water, and evaporated spontaneously. The residue is treated with a little water, one or two drops of sulphuric acid, and sufficient of a strong solution of potassium permanganate to ensure that the liquid shall remain red after standing for 24 hours in a closed tube. The odour of valeric aldehyde is frequently noticeable shortly after the addition of the permanganate, but the characteristic smell of *valeric acid*, on which this very delicate test is based, is not appreciable until after standing.

Determination.—Fusel oil containing not more than 15 p.c. of proof spirit is allowed to be delivered from distilleries in the United Kingdom or to be admitted on importation from abroad duty free.

Numerous methods have been suggested for the estimation of ethyl alcohol in fusel oil, but none is free from objection. The following method can be recommended as being sufficiently accurate for all practical purposes.

75 c.c. of the sample, with 150 c.c. of water, are shaken vigorously in a separator (A) for 4 or 5 minutes, and allowed to stand. If an emulsion forms, a few grains of salt are added. The aqueous layer is drawn off into a second separator (B) saturated with salt, and extracted with 150 c.c. of petroleum ether. The brine layer is then drawn off into a third separator (C) and extracted with a further 150 c.c. of petroleum ether, and the brine run off into a distilling flask.

The oil remaining in (A) is treated a second time with 150 c.c. of water, the aqueous layer drawn off into the petroleum ether in (B), saturated with salt, and extracted. The brine layer is drawn off into (C) and there extracted with the petroleum ether, from which, after separation, it is run into the distilling flask. The procedure described in this paragraph is then repeated.

The 450 c.c. of brine are distilled and the first 75 c.c. of distillate collected. This portion is saturated with salt and extracted with 150 c.c. petroleum ether. The brine is run off, distilled, 75 c.c. collected, and the specific gravity and refractometer (Zeiss immersion) reading of this fraction determined.

The refraction will be somewhat higher than that of ethyl alcohol of the same density. The difference is multiplied by the appropriate factor (1·1 is taken in ordinary cases), and the product is deducted from the percentage of proof spirit as deduced from the density of the distillate.

The accurate estimation of fusel oil in spirit is extremely difficult. A very rapid and simple process introduced by Traube is said to give satisfactory results where great accuracy is not required. The specific gravity of the spirit having been determined, sufficient water is added to reduce the proportion of alcohol to 20 p.c. The liquor is sucked up and allowed to fall a few times in a carefully dried, thin-sided capillary tube, 20 cm. long, and about 0·8 mm. in diameter, fastened to a graduated scale, and terminating at the zero in two points, which are set by a stand moved upon screws, to the surface of the liquid in the vessel into which the capillary tube dips. The height to which the liquid rises decreases with a rise in the proportion of fusel oil. From the observed height of the liquid in the capillary tube (temperature 21°), the percentage of fusel oil may be ascertained from the following table (Girard and Cuniasse, l'Analyse des Alcools):—

Height in tube	P.c. of fusel oil	Height in tube	P.c. of fusel oil
53·6 mm.	0·0	48·85 mm.	0·6
52·7 ,,	0·1	48·20 ,,	0·7
51·85 ,,	0·2	47·45 ,,	0·8
51·0 ,,	0·3	46·75 ,,	0·9
50·3 ,,	0·4	46·15 ,,	1·0
49·6 ,,	0·5		

This process is said to be largely affected by accidental conditions, such as temperature, moisture in the tube, &c., and by the presence of nitrobenzene, oils of peppermint, fennel, orange, and carraway, amyl acetate, &c.

Further information on this process is given by Traube (Bied. Zentr. 15, 559; Ber. 19, 892; Chem. News, 53, 302; Rep. Anal. Chem. 6, 659); Stutzer and Reitmair (*ibid.* 6, 606); Dingl. poly. J. 268, 126; and Girard and Cuniasse.

An improved apparatus, which he calls a *stalagmometer*, has been introduced by Traube (Ber. 20, 2644) for this estimation. The liquid, diluted as above to 20 p.c., is filled to a mark in a vessel, and is allowed to fall drop by drop through a capillary tube at the base of the vessel, the number of drops in a certain time being noted and compared with the number of drops of pure alcohol of the same strength falling in the same time from the same apparatus. A smaller proportion of fusel oil than 0·05 p.c. may thus be determined.

The following table serves to indicate the percentage of fusel oil corresponding with the number of drops observed (Girard and Cuniasse) :—

Number of drops	P.c. of fusel oil	Number of drops	P.c. of fusel oil
100	0·0	108·5	0·6
101·8	0·1	109·9	0·7
103·6	0·2	111·5	0·8
105·0	0·3	113·1	0·9
106·3	0·4	114·7	1·0
107·5	0·5		

If the temperature of the spirit is higher or lower than that for which the instrument has been calibrated, the number of drops observed is increased or diminished by 0·1 drop for every 30 drops for each degree of difference.

Another process, first introduced by Röse (Pharm. Centr. 1886, 9), depends on the alteration produced by the presence of fusel oils in the solubility of 50 p.c. alcohol in chloroform, and is said to be scarcely affected by the bodies which influence the results obtained by Traube's method. This process, which is official in Germany and Switzerland, has been modified at various times by Stutzer, Reitmair, Herzfeld, Windisch, and others (*vide* Zeitsch. anal. Chem. 34, 1895). Bromwell's modification of Röse's fusel-oil apparatus (*v.* U.S. Dept. Agric. Bur. of Chem. Bul. 46, 59) consists of a pear-shaped bulb holding about 200 c.c., stoppered at the upper end, and having at the lower end a graduated stem of about 4 mm. internal diameter leading to another bulb of about 20 c.c. capacity, and terminating in a tube provided with a stop-cock. The narrow stem is graduated in 0·02 c.c. from 20·0 to 22·5 c.c.

Fusel-free alcohol is first prepared by fractional distillation over caustic alkali to resinise aldehydes, saponify esters, and saturate acids, and is diluted to exactly 30 p.c. by volume (sp.gr. 0·965 at 15·6°); a quantity of chloroform is dehydrated and redistilled, and a solution of sulphuric acid of sp.gr. 1·2857 at 15·6° is prepared.

Of the sample under examination, 200 c.c. are taken, made alkaline, and distilled until about 175 c.c. are over. After cooling, 25 c.c. of water are added to the distilling flask, and the distillation resumed until 200 c.c. are collected. The distillate is diluted to exactly 30 p.c. by volume (sp.gr. 0·965 at 15·6°), and this, together with the Röse apparatus and the flasks containing the reagents (fusel-free alcohol, chloroform, and sulphuric acid), is placed in a water-bath kept exactly at 15° until all have acquired a uniform temperature.

The apparatus is then filled to the 20 c.c. mark with chloroform (through the lower tube by suction), and 100 c.c. of the fusel-free alcohol and 1 c.c. of sulphuric acid added. The apparatus is inverted and shaken vigorously for 2 or 3 minutes, the stop-cock being momentarily opened once or twice to equalise pressure. The apparatus is then allowed to stand for 10 or 15 minutes in the water-bath at 15°, with occasional turning to hasten the separation of the reagents, and the volume of the chloroform is noted.

The apparatus is then thoroughly cleaned and dried, and the operation repeated, using the distillate from the sample instead of the fusel-free alcohol. An increase in the volume of the chloroform is observed due to the fusel oil present, and this difference, multiplied by the factor 0·663, gives the volume of fusel oil in 100 c.c., or the percentage of fusel oil by volume in the 30 p.c. distillate. This is then calculated to the percentage of fusel oil by volume in the original sample according to the alcoholic strength of the latter.

For example, in a sample containing 50 p.c. of alcohol by volume, the increase in the chloroform volume with the distillate from the sample diluted to 30 p.c. being 1·62 c.c., and that in the fusel-free alcohol also at 30 p.c., 1·42 c.c., the difference is 0·20 c.c. The volume of fusel oil in 100 c.c. of the 30 p.c. distillate is, therefore, 0·20×0·663=0·1326 c.c., and the percentage of fusel oil by volume in the sample (50 p.c. alcohol by volume) is 0·1326×50÷30=0·221.

In France, the official method is that of *Savalle* as modified by Girard and Cuniasse, and is based upon the depth of colour obtained by the action of strong sulphuric acid upon the higher alcohols. The method, which at best gives only comparative results, and these only when conducted under conditions so strict as to be almost unattainable in practice, is as follows :—

50 c.c. of the brandy, after distilling to free from colouring and extractive matters, and adjusted to contain 50 p.c. of absolute alcohol, are placed in a flask of about 250 c.c. capacity, and 1 gram of metaphenylenediamine is added, together with a little pumice.

The flask is adjusted to a reflux condenser and the contents boiled gently for an hour and then allowed to cool. The contents of the flask are then distilled to near dryness, and the distillate made up to the original volume of 50 c.c. with a few drops of distilled water. 10 c.c. of the spirit thus prepared are placed in a thoroughly clean flask of about 75 c.c. capacity, and 10 c.c. of pure concentrated sulphuric acid are carefully run into the flask so that it forms a layer under the spirit. The contents of the flask are quickly mixed and heated over a Bunsen flame, with constant agitation for 15 seconds after the commencement of ebullition. The liquid is set aside to cool, the mouth of the flask being covered with a small watch-glass. One or more samples of standard alcohol of 50 p.c. strength, and containing known quantities of *iso*butyl alcohol (50 mg. or less per 100 c.c.) are treated in exactly the same way. When cold, the coloration given by the sample under examination is compared with those given by the standard samples.

Beckmann's method depends upon the separation of the higher alcohols from the spirit by means of calcium chloride and carbon tetrachloride, the conversion of the higher alcohols into their nitrites by the action of sodium nitrite and sodium bisulphite, removing the excess of nitrous acid with sodium bicarbonate, decomposing the nitrites with sulphuric acid, and final titration of the nitrous acid thus obtained with permanganate.

The details of this process are as follows :—

25 to 50 c.c. of the spirit, after distillation to free it from any colouring or extractive matter, are taken and diluted with water, so that the mixture shall contain not more than 20–25 p.c. of absolute alcohol. The solution is then saturated with sodium or calcium chloride, and extracted four times successively by vigorously shaking with 40 c.c., 25 c.c., 25 c.c., and 10 c.c. of carbon tetrachloride. The carbon tetrachloride extracts are mixed, and then washed three times successively by shaking with 50 c.c., 25 c.c., and 25 c.c. of saturated salt solution, and once with 25 c.c. of saturated sodium sulphate solution. The washings of each are extracted with 25 c.c. of fresh carbon tetrachloride, and this after separation is added to the first carbon tetrachloride extract. The mixed carbon tetrachloride solution is then dried by shaking vigorously with freshly heated calcium chloride in powder.

To the dried tetrachloride solution 3 grams sodium nitrite and 3 grams of sodium bisulphite are added, and the mixture is shaken occasionally during an hour. It is then filtered through glass wool, and to the filtrate 3 grams of sodium bicarbonate are added, and the mixture shaken occasionally during half an hour. Then 20 c.c. of water are added, and the whole gently shaken and allowed to stand till the mixture separates into two layers. The separated carbon tetrachloride is then run off. To the remainder, 10 c.c. of pure concentrated sulphuric acid are added; and, after shaking gently to mix, the mixture is poured into 100 c.c. of ice-cold water. The solution thus formed is titrated with standard permanganate (1 in 1000) until the pink colour becomes permanent. (The end reaction is not very sharp.)

(1 c.c. permanganate solution=0·00278 gram amyl alcohol.)

According to Schidrowitz (*v. infra*), this method, as published, is unreliable, owing chiefly to the extraction of ethyl alcohol by the carbon tetrachloride.

The best method hitherto suggested is that of Marquardt, as modified by Allen and Schidrowitz. It is based upon the oxidation of the higher alcohols into the corresponding acids, and the estimation of the latter by titration or by converting them into and weighing their barium salts.

The extraction is carried out as in the Beckmann process just described. To the washed carbon tetrachloride solution 5 grams of pure powdered potassium dichromate, 2 c.c. of concentrated sulphuric acid, and 10 c.c. of water are added. The mixture is shaken and gently boiled for 8 hours under a reflux condenser. It is cooled, a little pumice and 50 c.c. of recently boiled distilled water are added, and it is then distilled to near dryness. The residue is cooled, 50 c.c. water added, and again distilled.

The distillates are mixed and titrated with N/10-baryta solution, first with methyl orange as indicator, and then with phenolphthalein. The acid indicated by the methyl orange is regarded as 'mineral acid,' and the difference as organic acid, which is calculated into amyl alcohol by multiplying the number of c.c. of N/10-baryta solution by 0·0088, and the figure indicating the dilution of the alcohol.

To obtain the combining weight, the solution containing the barium salt of the acid is separated from the carbon tetrachloride, evaporated, filtered, and finally dried in a platinum capsule and weighed. The weighed residue is then treated with a slight excess of sulphuric acid, again evaporated, and the barium sulphate ignited and weighed. From the weights found the combining weight of the acid is calculated.

By this method also some ethyl alcohol is extracted by the carbon tetrachloride, but apparently it does not appear as acetic acid after oxidation, and, according to Schidrowitz, the effect attributed to 'mineral acid' (of the presence of which there is no proof) may be due to some action between the methyl orange and certain aliphatic acids present.

(For a detailed criticism of the last three methods described, *see* Schidrowitz and Kaye, Analyst, June, 1905, and June, 1906.) J. C.

FUSTIC, YOUNG, *v.* YOUNG FUSTIC.

FUSTIN *v.* GLUCOSIDES; also YOUNG FUSTIC.

FUSTIN TANNATE *v.* YOUNG FUSTIC.

G

G-ACID. 2-Naphthol-6 · 8-disulphonic acid.

GABBRO. A holocrystalline igneous rock composed essentially of basic plagioclase-felspar and augite, and containing less than about 50 p.c. of silica. It is the plutonic equivalent of the finer-grained dolerite and basalt, having crystallised slowly under considerable pressure from large bodies of molten material within the earth's crust. The felspar is the soda-lime labradorite or the lime-felspar anorthite; the augite is usually the laminated diallage variety; apatite, iron-ores (magnetite and ilmenite) are usually present in small amount. When the rhombic pyroxene hypersthene is present in addition to plagioclase and augite the rock is called a norite. The more acid quartz-gabbro forms a passage to diorite, whilst the more basic olivine-gabbro grades into the peridotites. The rock is dark grey, black, or greenish-black in colour, medium to coarse grained in texture, and very hard. Sp.gr. 2·7–3·0 (weight per cubic foot 170–190 lbs.); crushing strength 640–2200, averaging 1830 tons per sq. ft.

Analysis I of olivine-gabbro from Skye; also Cr_2O_3 trace (W. Pollard, 1900). II, olivine-gabbro from Lizard, Cornwall; also Cr_2O_3 0·08, V_2O_3 0·02, Li_2O trace, FeS_2 0·11 (E. G. Radley, 1912). III, Quartz-gabbro from Carrock Fell (G. Barrow, 1894). IV, Kentallenite from Kentallen, Argyllshire; also

Cr_2O_3 0·10, (Co,Ni)O 0·07, CO_2 0·16; Cl trace (W. Pollard, 1900).

	I.	II.	III.	IV.
SiO_2 . .	46·39	50·69	53·50	52·09
TiO_2 . .	0·26	0·42	0·45	0·73
Al_2O_3 . .	26·34	20·56	22·20	11·93
Fe_2O_3 . .	2·02	1·55	3·60	1·84
FeO . .	3·15	3·10	2·64	7·11
MnO . .	0·14	0·16	0·35	0·15
CaO . .	15·29	11·99	9·45	7·84
MgO . .	4·82	6·84	2·00	12·48
K_2O . .	0·20	nil	0·61	3·01
Na_2O . .	1·63	3·36	4·26	0·24
P_2O_5 . .	0·58	0·05	—	0·34
H_2O . .	trace	1·12	1·50	0·35
	100·82	100·05	100·59	100·24
Sp.gr. . .	2·85	—	2·80	2·94

Gabbro forms large masses and is of wide distribution, occurring, for example, in the Highlands of Scotland, Lendalfoot in Ayrshire, Carrock Fell in Cumberland, North and South Wales, the Lizard district in Cornwall, and in Guernsey. Owing to its dull colour and difficulty of working, it is not very extensively employed as a building stone; and it is reputed not to weather well, especially those varieties containing more felspar. In the trade it often passes under the name of 'black granite' (on the other hand, the trade name 'Norwegian gabbro' is sometimes applied to the augite-syenite—laurvikite—from the south of Norway). Medium-grained varieties are used for road metal and paving-sets. Olivine-gabbro is extensively quarried for export at Herrestad near Kärda in prov. Jönköping, Sweden, and on the Pleasant river near Addison in Maine. The 'black granite' of the Kentallen quarries in Argyllshire is a dark bluish-grey, medium-grained alkali-gabbro containing orthoclase, olivine, and biotite in addition to the usual constituents, and has been named kentallenite. It is used principally for paving-sets, and on a polished surface it displays bright plates of mica.

Gabbro takes a good polish and is sometimes used for ornamental purposes. The diallage often displays a metallic sheen, and in the gabbro of Volhynia and near Kiev in Russia the labradorite sometimes shows blue reflections. Coarse-grained gabbros when partly altered show the light- and dark-coloured minerals in marked contrast, and have been used as far back as Roman times as ornamental stones. In some cases the felspar is altered to saussurite and the diallage to emerald-green smaragdite, the rock being then known as euphotide; this beautiful ornamental stone occurs in the Alps, Corsica ('Verde di Corsica'), and Elba. A dark-coloured orbicular gabbro from Dehesa, San Diego Co., California, has also been used as an ornamental stone.

Magmatic segregations of iron-ores, metallic sulphides (nickeliferous pyrrhotite and copper-pyrites), and apatite sometimes occur in connection with gabbro masses. L. J. S.

GADININE *v.* PTOMAÏNES.

GADOLINITE. A rare mineral consisting of silicate of yttrium earths, glucina, and ferrous oxide $Gl_2FeY_2Si_2O_{10}$. Analyses show about 40–45 p.c. of yttrium earths of molecular weight 250–290; the amount of erbia has been separately determined as 10–15 p.c. It occurs in much larger masses than the other rare-earth minerals, forming rough, black, and opaque crystals, sometimes exceeding 20 kilos. in weight. The crystals are monoclinic with an orthorhombic aspect; but in thin sections the material is optically isotropic. When heated, the mineral suddenly glows brightly, a molecular transformation taking place; the material then becomes optically birefringent, increases in sp.gr. (from 4·1–4·4 to 4·3–4·7), and changes in colour (as seen in sections) from greenish to reddish. Gadolinite occurs in some abundance as masses of considerable size in pegmatite veins at a few localities; notably, at Ytterby and near Fahlun in Sweden; in the felspar quarries of Sætersdalen and Hitterö, and elsewhere in the south-east of Norway; in Llano Co., Texas, Mohave Co., Arizona, and Western Australia. The locality (Barringer Hill, five miles south of Bluffton) in Llano Co. has yielded masses of gadolinite weighing 200 lbs., in association with several other rare-earth minerals. These have been worked for the supply of yttrium and erbium earths used in the 'glower' of the Nernst lamp (W. E. Hidden, Amer. J. Sci. 1889, 38, 474; 1905, 19, 425). L. J. S.

GADOLINIUM. Gd = 157·3 (*cf.* Urbain, Compt. rend. 1905, 140, 583). This element was first identified by Marignac in 1880, who separated its salts from those of other rare-earth metals present in samarskite by fractional precipitation with potassium sulphate (Arch. de Genève, 1880, [3] 3, 413; Compt. rend. 1880, 90, 899). With europium and terbium, gadolinium forms the small group of terbium metals, and as the solubilities of its salts are intermediate between those of the other two members of the family, the final separation of gadolinium from these elements is a matter of considerable difficulty. The older methods of separation, precipitation by ammonia, crystallisation of the oxalates, formates, and double sulphates, or combinations of these processes, did not, in all probability, lead to the complete purification of gadolinium. *Cf.* Meyer and Müller, Zeitsch. anorg. Chem. 1919, 109, 1, who have examined the efficiency of the various methods of separation. The presence of small quantities of terbium is indicated by a faint yellow discoloration of the colourless gadolinia. Europium is indicated spectroscopically in the arc spectrum.

Sources. The crude yttrium earths from monazite sand, samarskite, ytterbite (gadolinite), xenotime, æschynite, &c.

Extraction and separation of the terbium earths. The first four methods outlined below serve rather to concentrate the terbium earths than to separate them from one another, gadolinium being the only one of the three which is obtained by these processes in a moderately pure condition.

A convenient starting-point for the separation of the terbium earths is the most soluble fraction of the ammonium or magnesium double nitrate separation of the rare earths. The preliminary elimination of the cerite metals with sodium or potassium sulphate is less preferable, since it involves a co-precipitation of a portion of the terbium group.

1. *Fractional precipitation with ammonia.*—In this process, terbia accumulates in the first fractions, followed successively by samaria and

gadolinia. Accordingly, samaria is a weaker base than gadolinia, and this relationship forms an exception to the rule that the more electropositive earths yield less soluble double sulphates and nitrates than the less electro-positive oxides (*cf.* Lecoq de Boisbaudran, Compt. rend. 1890, 111, 394; Bettendorf, Annalen, 1892, 270, 376; Benedicks, Zeitsch. anorg. Chem. 1900, 22, 393).

According to Katz and James (J. Amer. Chem. Soc. 1914, 36, 779), in separating gadolinium from samarium by fractional precipitation with ammonium hydroxide the samarium would be concentrated in the last fractions, instead of in the early fractions, as stated by Boisbaudran and Benedicks.

Jordan and Hopkins (J. Amer. Chem. Soc. 1917, 39, 2614) recommended first to remove cerium by the bromate method and fractionally crystallise the residue. The less soluble fractions contain only europium, samarium, gadolinium, and neodymium, which are converted into the dimethyl phosphates and again fractionated. The least soluble fractions will then consist mainly of gadolinium. The last traces of samarium can be removed by precipitation with sodium glycollate.

2. *Fractional crystallisation of the sodium and potassium double sulphates.*—In isolating gadolinia from samarskite, Marignac (*l.c.*) separated the less basic constituents of the yttrium earths by partially decomposing the nitrates, dissolved the oxides, consisting chiefly of yttria, samaria, and the terbium earths in nitric or hydrochloric acid, and precipitated fractionally with potassium sulphate solution. After a systematic course of fractionation, he obtained the following four fractions in descending order of solubility: (i.) yttrium, terbium; (ii.) gadolinium, purified by further fractionations with potassium sulphate; (iii.) samarium, didymium; (iv.) didymium (*cf.* Delafontaine, Arch. de Genève, 1878, 61, 273; Ann. Chim. 1878, [5] 14, 238; Lecoq de Boisbaudran, Compt. rend. 1883, 97, 1463; Bettendorf, *l.c.*).

3. *Fractional crystallisation of formates and oxalates.*—The sparing solubility of the formates of the terbium group has been utilised in the separation of these metals, these salts separating as white microcrystalline powders from the concentrated solutions (*cf.* Delafontaine, *l.c.*; Marignac, *l.c.*; Hofmann and Krüss, Zeitsch. anorg. Chem. 1893, 4, 27; Feit, *ibid.* 1905, 43, 267).

The terbium earths can also be separated from erbium and yttrium by precipitation with oxalic acid in nitric acid solution (Marignac and Delafontaine, *l.c.*).

4. *Fractional crystallisation of the ethyl sulphates.*—The systematic crystallisation of the ethyl sulphates of the rare earths from water or alcohol leads to a separation of the three principal groups; cerite earths, terbium earths, and yttrium earths, arranged in descending order of solubility (Urbain, Ann. Chim. 1900, [7] 19, 184).

5. *Fractional crystallisation of the nitrates.*—The more complete separation of the constituents of the terbium group has been accomplished by the use of the nitrates and double nitrates. By fractionating the nitrates of terbium earths containing samaria, the sparingly soluble gadolinium nitrate and the more readily soluble samarium nitrate were separated as well as a middle fraction rich in europium. The solubility of the rare-earth nitrates falls from lanthanum to samarium, attaining a minimum at gadolinium, and rises again till it reaches ytterbium.

By a lengthy fractionation of the nitrates from nitric acid (sp.gr. 1·3), Demarçay isolated small quantities of europium and gadolinium in a highly purified condition (Compt. rend. 1900, 130, 1469; 131, 343; 1901, 132, 1484). A further improvement in the separation was effected by Urbain and Lacombe (*v.* EUROPIUM), who crystallised the double magnesium nitrates of the rare earths in the presence of magnesium bismuth nitrate.

After crystallisation of the samarium and bismuth double salts, the mother liquor contains europium and gadolinium, the former being the first to separate on further fractionation. The gadolinium is then separated from the other remaining earths by fractionating the simple nitrates in the presence of bismuth nitrate. The latter salt now causes a separation to occur between gadolinium and dysprosium, the middle fraction consisting of bismuth and terbium nitrates. In this way, gadolinium is completely freed from terbium, dysprosium, and erbium earths. The fractional crystallisation of the nickel double nitrates of the terbium earths has led to a similar separation (*cf.* Compt. rend. 1903, 137, 568, 792; 1904, 138, 84, 627; 139, 736; 1905, 140, 1233; 141, 521).

The best starting materials for the preparation of gadolinium compounds are euxenite, samarskite, or the monazite residues, beginning with several kilos. of material.

The following method of procedure is recommended for the purification of gadolinium compounds: (1) If the rare earth mixture contains little cerium earths and much yttrium earths the gadolinium is separated with the cerium earths in one operation by the potassium double sulphate method. (2) If the mixture contains much cerium earths the major portion of these is separated by the double nitrate method. In either case a fraction very much richer in gadolinium is obtained. This is converted into the bromates and the yttrium earths removed by fractionation. The ytterbium earths first pass into the mother liquors, then follow the erbium earths, and last of all yttrium. It is essential that the yttrium should be removed at this stage, for it is scarcely possible to separate it at any of the remaining stages. The main fraction contains samarium, gadolinium, neodymium, terbium and europium; it is converted into acetate and fractionated, the fractionation being combined with the fractionation of the double bismuth nitrates. The cerium earths are rapidly separated, and a brown mixture of oxides, containing gadolinium and terbium is obtained. These salts are rapidly separated by fractional precipitation with ammonia (Meyer and Müller, Zeitsch. anorg. Chem. 1919, 109, 1).

Compounds. The oxide and chloride of gadolinium are colourless; the solutions of the latter have no selective absorption in the visible region of the spectrum, but show four strong bands in the ultra-violet end. (For spark-spectrum, *v.* Compt. rend. 1890, 111, 472; 1896, 122, 728; 1900, 131, 343; 1905, 140, 1233; 141, 521, 954;

Ber. 1901, 34, 2460; Annalen, 1891, 263, 164. For arc-spectrum, *v.* Eberhard, Zeitsch. anorg. Chem. 1905, 45, 394; Exner and Haschek, Die Wellenlängen der Bogenspektra, 1904.)

The spectrum of gadolinium contains seven groups of lines which are characterised by constant differences between the wave-lengths of corresponding members of the several groups (Poulson, Physikal. Zeitsch. 1915, 16, 7).

Gadolinia (*Gadolinium oxide*) Gd_2O_3, a white amorphous hygroscopic powder, absorbing carbon dioxide from the air; sp.gr. 7·407 at 15°.

Gadolinium chloride and **bromide** $GdCl_3,6H_2O$ and $GdBr_3,6H_2O$, soluble deliquescent salts, the former yielding the yellow double chlorides, $GdCl_3{\cdot}PtCl_4,10H_2O$, and $GdCl_3{\cdot}AuCl_3,10H_2O$.

Gadolinium fluoride GdF_3, a white gelatinous precipitate becoming granular on heating on the water-bath; somewhat soluble in hot hydrofluoric acid.

Gadolinium cobalticyanide

$$Gd_2(CoC_6N_6),9H_2O$$

Sparingly soluble in 10 p.c. solution of hydrochloric acid. 1000 parts of saturated solution contain 1·86 part of the salt.

Gadolinium platinocyanide

$$2Gd(CN)_3{\cdot}Pt(CN)_2,18H_2O;$$

separates in red rhombic crystals with a green reflex; it resembles the isomorphous platinocyanides of yttrium and erbium, and differs from the corresponding double salts of the cerium group, which are yellow with a blue reflex.

Gadolinium nitrate $Gd(NO_3)_3,6H_2O$ or $5H_2O$, m.p. 91°–92°, is of all the nitrates of the rare earths the least soluble in nitric acid (*cf.* Demarçay, Compt. rend. 1900, 131, 343; *v.* Lang and Haitinger, Annalen, 1907, 351, 450). The following double nitrates:

$$2Gd(NO_3)_3{\cdot}3Mg(NO_3)_2,24H_2O$$

and $2Gd(NO_3)_3{\cdot}3Ni(NO_3)_2,24H_2O$, have been utilised in the isolation of gadolinium; the former melts at 77°.

Gadolinium sulphate $Gd_2(SO_4)_3,8H_2O$ separates from hot solutions in monoclinic crystals, isomorphous with yttrium sulphate.

Gadolinium hydrazine sulphate

$$Gd_2(SO_4)_3{\cdot}(N_2H_5)_2SO_4,3H_2O,$$

separates in colourless, sparingly soluble crystals when a solution of the mixed sulphate is boiled for some time.

Gadolinium sulphide Gd_2S_3, a yellow hygroscopic mass, sp.gr. 3·8, is produced by heating the sulphate in hydrogen sulphide; it is slowly decomposed by water.

Gadolinium acetate $Gd(H_3C_2O_2)_3,4H_2O$ forms moderately soluble triclinic crystals; the **Oxalate** $Gd_2(C_2O_4)_3,10H_2O$ separates from nitric acid solution in monoclinic crystals (*v.* Brauner, Chem. Soc. Trans. 1898, 73, 951); the **Malonate** $Gd_2(H_2C_3O_4)_3,8H_2O$ is obtained in refractive yellow needles (*v.* Erdmann and Wirth, Annalen, 1908, 361, 190).

Dimethyl phosphate, long, white needles, solubility 23·0 at 25° and 6·7 at 95°.

For other salts of gadolinium, *see* Bissel and James, J. Amer. Chem. Soc. 1916, 38, 873; Jantsch and Grünkraut, Zeitsch. anorg. Chem. 1913, 79, 305; Armstrong and Rodd, Proc. Roy. Soc. 1912, 87, 204; Katz and James, J. Amer. Chem. Soc. 1913, 35, 872; Morgan and James, *ibid.* 1914, 36, 10. G. T. M.

GAHNITE or **ZINC-SPINEL.** Zinc aluminate $ZnAl_2O_4$, crystallised in the cubic system and belonging to the spinel group of minerals. According to the formula it contains 44·3 p.c. ZnO (35·6 p.c. Zn), but this is usually partly replaced isomorphously by ferrous oxide, manganous oxide, and magnesia, whilst the alumina may be partly replaced by ferric oxide. The mineral usually occurs as grey or dark greenish-black, opaque octahedra. Sp.gr. 4·5–4·9; H. 7½–8. It occurs as crystals embedded in talc-schist at Fahlun in Sweden, and more abundantly in crystalline limestone with other zinc ores (willemite and franklinite) at Franklin Furnace and Sterling Hill in New Jersey. It is also found at Bodenmais in Bavaria (with pyrrhotite), in Massachusetts, and a few other localities; and has also been observed in the muffles of zinc furnaces. The mineral was named in 1807 after the Swedish chemist, J. G. Gahn (1745–1818). L. J. S.

GALACTIN *v.* GUMS.

GALACTOSE *v.* CARBOHYDRATES.

GALAFATITE. An aluminium potassium sulphate, named after the discoverer, found, amongst other places in Spain, at Benahabux near Almeria, where it occurs in parallel veins from 5 to 6 mm. thick. It is white when pure, has a sp.gr. 2·75, and hardness 3·5. It is treated by calcination, followed by lixiviation with water, whereby a solution of potassium sulphate and a residue of nearly pure alumina are obtained. The calcined ore contains 65–70 p.c. of alumina and 25–30 p.c. of potassium sulphate (Preuss, Eng. and Min. J. 1911, 91, 261; J. Soc. Chem. Ind. 1911, 30, 282).

GALALITH or **ERINOID.** Artificial horn prepared by the action of formaldehyde on casein. Skim milk is treated with caustic alkali or alkali carbonate, the casein is precipitated by the action of rennet, pressed, impregnated with formaldehyde and dried (J. Soc. Chem. Ind. 1909, 101). Is used as an insulator and as a non-inflammable substitute for ivory, amber, tortoise-shell, coral, bone, ebony, &c. Is employed in electrical work, for aeroplanes, in the manufacture of buttons, pianoforte keys, &c. (*see* CASEIN).

GALANACK. A mixture of sulphur, tar and oil used as a cement or lute.

GALANGA ROOT. Galanga root is the rhizome of *Alpinia officinarum* (Hance), and is a native of China. It is employed in the form of a decoction as a remedy for dyspepsia.

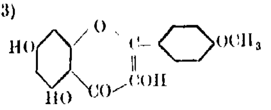
Galanga root was first examined by Brandes (Arch. Pharm. [2] 19, 52), who isolated from it a substance which he named kæmpferide, but this, according to Jahns (Ber. 1881, 14, 2385), was a mixture of three substances, kæmpferide, alpinin, and galangin. The subject was later examined by Gordin (Dissert. Berne, 1897), and by Ciamician and Silber (Ber. 1899, 32, 861) and Testoni (Gazz. chim. ital. 1900, 30, ii. 327), and it is now clearly demonstrated that galanga root contains kæmpferide, galangin, and galangin monomethylether. According to Testoni, the alpinin of Jahns is a mixture of galangin and kæmpferide.

Kæmpferide $C_{16}H_{12}O_6$ consists of yellow needles, m.p. 227°–229°, soluble in alkaline solutions with a yellow colour. Sulphuric acid gives a blue fluorescent yellow solution.

Triacetylkæmpferide $C_{16}H_9O_6(C_2H_3O)_3$, colourless needles, m.p. 193°–194° (Ciamician and Silber and Testoni) (*cf.* also Jahns), *tribenzoylkæmpferide* $C_{16}H_9O_6(C_7H_5O)_3$, m.p. 177°–178° (Testoni), *kæmpferide diethylether*

$$C_{16}H_{10}O_6(OC_2H_5)_2$$

(Testoni), yellow needles, m.p. 137°–139°, and *dibromkæmpferide* $C_{16}H_{10}Br_2O_6$, yellow needles, m.p. 224°–225° (decomp.) (Jahns) have been prepared. In the presence of acetic acid, kæmpferide yields, by means of mineral acids, yellow crystalline compounds, and alcoholic potassium acetate gives *monopotassium kæmpferide* $C_{16}H_{11}O_6K,H_2O$, yellow needles, which is decomposed by boiling water (Perkin and Wilson, Chem. Soc. Trans. 1903, 83, 136) Kæmpferide is in reality *kæmpferol monomethylether* (v. Kostanecki and Rozycki, Ber. 1891, 24, 3723)



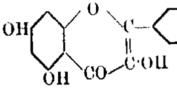
For a detailed description of kæmpferol, *see* *Delphinium consolida.*

Galangin $C_{15}H_{10}O_5$, the second constituent of galanga root, crystallises in yellowish-white needles, m.p. 214°–215°, soluble in alkaline solutions with a yellow colour. With acetic anhydride, it gives a *triacetyl* derivative

$$C_{15}H_7O_5(C_2H_3O)_3$$

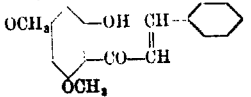
m.p. 140°–142° (Jahns), and by means of methyl iodide a *dimethylether* $C_{15}H_8O_3(OCH_3)_2$, m.p. 142°.

Galangin gives crystalline compounds with mineral acids in the presence of acetic acid, and reacts with alcoholic potassium acetate, yielding *monopotassium galangin*, yellow needles (Perkin and Wilson). When fused with alkali, *phloroglucinol* and *benzoic acid* are obtained. Galangin is a *dihydroxyflavonol*



and has been synthesised by v. Kostanecki and Tambor (Ber. 1899, 32, 2260) by a series of reactions similar to those employed in the preparation of kæmpferol.

2-Hydroxy-4 : 6-dimethoxychalkone

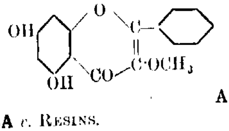


was converted into the corresponding flavanone, and the latter into its *iso*nitroso derivative. This compound, on boiling with dilute sulphuric acid, gave 1 : 3-dimethoxyflavonol, which, when heated with hydriodic acid, was transformed into galangin. Galangin dyes with mordanted woollen cloth the following shades :—

Chromium	*Aluminium*	*Tin.*	*Iron*
Olive-yellow.	Yellow.	Lemon-yellow.	Deep olive.

Galangin monomethylether $C_{15}H_9O_4(OCH_3)$, was first isolated from galanga root by Testoni (*l.c.*). It crystallises from methyl alcohol in bright yellow prisms, melts at about 300°, and dissolves in strong alkaline solutions with a yellow colour. *Diacetylgalangin monomethylether* $C_{16}H_{10}O_5(C_2H_3O)_2$ forms yellowish-white leaflets, melting at 175°–176°.

When air is aspirated through an alkaline solution of galangin monomethylether, it is oxidised with formation of *benzoic acid* and *phloroglucinol* (Perkin and Allison), and therefore possesses the constitution

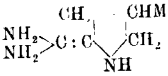


A. G. P.

GALBA *v.* Resins.

GALBANUM *v.* Gum resins.

GALEGINE $C_6H_{13}N_3$ is a crystalline alkaloid, m.p. 60°–65°, obtained by G. Tanret (Compt. rend. 1914, 158, 1182, 1426; Bull. Soc. chim. 1914, [iv.] 15, 613) from the seeds of *Galega officinalis.* It is optically inactive, and splits on heating with barium hydroxide solution into equal molecules of urea and 3-methylpyrrolidine. The constitution suggested is:



Galegine is moderately poisonous (Tanret, Compt. rend. 1914, 159, 108), and *Galega* has occasionally caused cattle poisoning. G. B.

GALENA (Ger. *Bleiglanz*; Fr. *Galène*). Native lead sulphide (PbS), the principal ore of lead (86·6 p.c.). It crystallises in the cubic system, and possesses three directions of perfect cleavage parallel to the faces of the cube. Well-developed crystals, with the form of the cube or cubo-octahedron, are not uncommon. The massive mineral is always readily recognised by its rectangular stepped cleavages with smooth and brilliant surfaces and a lead-grey colour; small broken fragments have the form of cubes or dice. Further, it can be readily scratched with a knife (H. 2½) yielding a black powder, and it is very heavy (sp.gr. 7·5). Ore with a very fine-grained texture may present somewhat the appearance of steel.

The presence of small quantities of silver in galena is of importance; though usually not more than a few ounces per ton in amount, it may reach 1 p.c. It is probably present in solid solution as silver sulphide, since argentite (*q.v.*) is isomorphous with galena. Examining polished surfaces of galena by reflected light under the high powers of a microscope, A. M. Finlayson (Quart. J. Geol. Soc. 1910, 66, 319) was able to detect fine strings of native silver running along the cleavage cracks of the galena. This was, however, only detected in specimens taken from the higher levels within reach of surface waters; specimens taken from deeper levels, where there has been no secondary alteration, showed no native silver. F. N. Guild (Econ. Geol. 1917, 12, 297) found that galena containing 0·10 to 0·35 p.c. silver shows definite spots of tetrahedrite and argentite; whils specimens containing more silver show evidence of later addition of ruby-silver, etc., in the form of veinlets.

Galena occurs chiefly in veins traversing rocks of various kinds, and also filling cavities in limestone. It is abundant in all lead-mining districts, and by its alteration it gives rise to cerussite, anglesite, and other secondary lead-bearing minerals. The use of galena for glazing pottery gave rise to the names 'potters' ore,' alquifoux (Fr.), and archifoglio (Ital.). The powdered mineral is used as a cosmetic by the natives of Nigeria. L. J. S.

GALIPOT *v.* Resins.

GALIUM. The roots of various species of galium have been employed to some extent for dyeing red on aluminium mordant, and Bancroft, in his Philosophy of Permanent Colours (vol. ii. 303), mentions six of these plants, the roots of which gave an excellent red in this manner. More especially he refers to the *Galium tinctorium*, the roots of which, about 2 feet in length, are of a dark reddish colour, and which were employed by the French inhabitants of Canada to dye their cloths red.

This product is also referred to by Hellot as a species of madder brought from Canada which possesses an extremely slender root and produces nearly the same effect as European madder.

According also to Bancroft, the roots of the nearly allied species of *Asperula*, of which he specially mentions the *Asperula tinctoria* known as 'Dyer's woodruff,' were at one time used for dyeing red instead of madder.

Of others may be mentioned the *Galium mullugo*, Great Ladies' bedstraw or Wild madder, *Galium verum*, Yellow Ladies' bedstraw, and *Galium aparine*, the well-known Cleaver's or Goose grass, the two latter of which are common to this country. The roots of this last certainly give a small amount of dye soluble in alkali with a purple colour, and there seems to be little doubt that all contain dyes which are fast to light and of the alizarin type, though they appear to give a somewhat yellower shade than alizarin itself. An examination of these in case they yield either anthrapurpurin or flavopurpurin would be interesting. A. G. P.

GALL-NUTS or **GALLS** or **Oak Apples**. (*Noix de Galle*, Fr.; *Gallen*, *Gallapfeln*, Ger.)

Galls are excrescences induced on plants by the attacks of animals (especially insects) or of other plants (especially fungi), which stimulate plant tissue that is capable of growing and cause hypertrophy. When an insect is the organism responsible, it usually infects very young parts (of roots, stems, or leaves), in which it deposits eggs from which there develop inside the gall larvæ and eventually mature insects.

The oak apples are thus caused by various species of gall wasps (*Cynipida*). The most important of these are those of north-temperate Europe and of the Levant. Of the former, one of the commonest on the common oak *Quercus sessiflora* (Salisb.) and *Q. pedunculata* (Ehrh.) is caused by *Cynips kollari*, and is like a yellowish-brown marble in size and shape, contains one central chamber, and eventually shows one little exit hole through which the insect has escaped.

More important are the Levant galls, induced on scrubby oaks belonging to the species *Q. lusitanica* (Lam.) [*Q. infectoria* (Oliver)], which occurs in the region extending from Greece, through Asia Minor, to Persia. The insect responsible is *Cynips tinctoria* (Htg.); this causes a gall by laying an egg in the young stem, which thereafter, by cell division and growth, swells into a gall in which the larva develops. The resultant insect may die inside the gall, or may bore its way out and escape through an exit hole. Levant galls are spherical to pear-shaped; the half near the stalk usually has a smooth surface, often inclined to be glossy, whereas the distal half is raised into lumps which are often conical in shape.

The Levant gall is very rich in tannin. Manceau found that the chemical composition in percentages was: water 12·05, ligneous substances 19·2, tannin 58·52, other constituents 10·21.

Levant galls vary in quality according to the region of origin, time of collection (including the condition as to whether gathered before or after the insects escape). The best kinds come from the Aleppo district: those gathered first, namely, in August or September, are of the highest quality, and are green, but subsequently become dark-coloured and harder: those gathered somewhat later are white, while the galls allowed to hang until winter are reddish-brown. Three qualities of Levant galls may be distinguished: (i.) Aleppo galls, small (2·5 cm. in diameter), dark-green to black in colour; (ii.) lighter-coloured galls, presenting the appearance of having been powdered on the surface; (iii.) Smyrna galls, larger (3–5 cm. in diameter), usually yellowish in tint. In water, the dark-hued galls sink, whereas the inferior lighter-tinted galls (even when dyed to imitate the former) float.

Galls (oak apples) of the same type are obtained in Southern Europe from scrubby specimens of *Quercus sessiliflora* (Salisb.) and *Q. pubescens* (Willd.).

GALLACETOPHENONE *v.* Ketones.

GALLAMINE BLUE, GALLANILIC BLUE, -VIOLET *v.* Oxazine colouring matters.

GALLEÏN. *Anthracene violet* (*v.* Alizarin and allied colouring matters).

GALLIC ACID, 3:4:5-*Trihydroxybenzoic acid* $C_6H_2(OH)_3COOH$, occurs in sumach, divi divi, Chinese tea, and various other plants (Stenhouse, Annalen, 45, 9; Hlasiwetz and Malin, Zeitsch. Chem. 1867, 271; Kawalier, J. 1852, 683; Perkin and Gunnell, Chem. Soc. Trans. 1896, 1307; Easterfield, *ibid.* 1901, 122; Grüttner, Arch. Pharm. 236, 293). Formed from tannin by boiling with dilute sulphuric acid, or when solutions of tannin become mouldy (Nierenstein, Chem. Zeit. 33, 126; Ber. 1910, 628), or by heating tannin with zinc (Iljin, J. pr. Chem. 80, [2] 332). In order to prepare it, finely powdered gall-nuts are macerated for some days with cold water, and the decanted liquid is exposed to the air and allowed to become covered with mould. An addition of yeast is advantageous. The gallic acid, which separates, is purified by recrystallisation from boiling water (Wittstein, J. 1853, 435; Tieghem, Zeitsch. Chem. 1868, 222; Scheele and Steer, J. 1856, 482). Heinemann (Fr. Pat. 314863; J. Soc. Chem. Ind. 1902, 415) boils the aqueous extract of galls with 5 p.c. by weight of sulphuric acid for about 5 hours. The reaction is complete when a drop of the solution gives no precipitate with a gelatin solution (*v.* also Soc. Anon. Manuf. de Prod. Chimiques et Pharm. J. Soc. Chem. Ind. 1900, 553). It is soluble in 3 parts of boiling, in 130 parts of cold water; crystallises in silky needles or triclinic prisms from water with 1 mol. H_2O, which it loses at 120°; is most readily soluble in acetone (Rosenheim and Schidrowitz, Chem. Soc. Trans. 1898, 882); melts at 222°–240°; and when heated to a higher temperature decomposes into carbon dioxide and pyrogallol (Braconnot, Annalen, 1, 26; Pelouze, *ibid.* 10, 159; Liebig, *ibid.* 101; 47; de Luynes and Esperandiew, Zeitsch. Chem 1, [2] 702; Thorpe, Pharm. J. 11, [3] 990). By heating equal weights of gallic acid and aniline, gallanilide is formed, which may be used as a germicide. It is non-toxic. When gallic acid is heated with twice its weight of aniline, and the aniline pyrogallate thus formed is boiled with benzene, pure pyrogallol is obtained (Cazeneuve, Bull. Soc. chim. 7, [3] 549; 11, 81, 82; Compt. rend. 117, 47). By the destructive distillation of ethyl gallate, pyrogallol, ethyl alcohol, and *rufigallic acid* (hexahydroxyanthraquinone) are produced (Perkin, Chem. Soc. Proc. 1902, 254). Rufigallic acid is also formed when gallic acid is heated with concentrated sulphuric acid (Robiquet, Annalen, 19, 204; Wagner, Chem. Zentr. 1861, 47; Löwe, J. pr. Chem. [i.] 107, 296; Jaffé, Ber. 1870, 694; Klobukowski and Noelting, *ibid.* 1875, 819; 1876, 1256; 1877, 880; Widmann, *ibid.* 1876, 856), and on reduction with sodium amalgam yields *alizarin* (Widmann, *l.c.*; Bull. Soc. chim. 24, [2] 359). By heating a mixture of gallic and benzoic acids with sulphuric acid, *anthragallol* (trihydroxyanthraquinone) is produced (Seuberlich, Ber. 1877, 39).

Gallic acid, on oxidation with nitric acid, chlorine, or copper sulphate and alkali, yields oxalic acid as the main product (Boettinger, Annalen, 257, 248; 260, 337; Biétrix, Compt. rend. 122, 1545); oxidation with persulphates in the presence of acetic and sulphuric acids, yields *ellagic acid* (Perkin, Chem. Soc. Trans. 1905, 1412), and in the presence of dilute sulphuric acid, *flavellagic acid* (Perkin, *ibid.* 1906, 252); electrolytic oxidation with potassium ferricyanide in the presence of sodium acetate or other electrolytes, yields purpurogallincarboxylic acid (A. G. and F. M. Perkin, *ibid.* 1904, 254; 1908, 118; Perkin and Nierenstein, *ibid.* 1905, 1429); oxidation in alkaline solution yields *galloflavin*. Gallic acid is not reduced appreciably in acid or neutral solution, but in alkaline solution, benzoic acid is formed (Gardner and Hodgson, Chem. Soc. Proc. 1908, 272; Guignet, Compt. rend. 113, 200). Gallic acid and its derivatives undergo condensation with nitrosodialkylanilines to form dyestuffs of the *oxazine* or *gallo-cyanine group* (Patent Literature, Frdl. i. 267–270; ii. 158, 167–173; iv. 485, 506; *v.* also OXAZINE COLOURING MATTERS); with *o*-nitrosonaphthols or *o*-aminonaphthols to form brown dyestuffs used in tanning (Ashworth and Sandoz, Ger. Pat. 75633, 75634; Frdl. iv. 504, 505); with salicylic acid by means of phosphorus oxychloride to produce *salitannol*, an antiseptic used for dressing wounds (Bayer & Co., Eng. Pat. 9898; J. Soc. Chem. Ind. 1898, 487; Dœbner, Ger. Pat. 94281; Chem. Zentr. 1898, i. 229); with acetaldehyde and benzaldehyde, yielding compounds which become coloured when dissolved in acids (Kahl, Ber. 1898, 151); with acetic acid and acetic anhydride to yield mono- and di- acetyl derivatives of gallic anhydride. These substances are insoluble in alkali, and so can be used instead of tannin for medicinal purposes, as the latter is soluble in the stomach juices (Bayer & Co., Eng. Pat. 1228; J. Soc. Chem. Ind. 1895, 297). Gallic acid is also used in the preparation of *thionine* dyestuffs (Nietzki, Ger. Pat. 73556, 76923, 79172; Frdl. iii. 360; iv. 455, 456).

Gallic acid condenses with formaldehyde to yield four distinct methylenedigallic acids, yielding dyestuffs on treatment with nitrosulphuric acid in sulphuric acid solution (Möhlau and Kahl, Ber. 1898, 259). It forms compounds with albuminoids (Wörner, Ger. Pat. 189334; J. Soc. Chem. Ind. 1908, 644), and with ferments (Ger. Pat. 198305; J. Soc. Chem. Ind. 1908, 713). It is absorbed by organic colloids, this being of interest, since it bears on the theory of dyeing and tanning processes (Dreaper and Wilson, J. Soc. Chem. Ind. 1906, 515). Complex salts of gallic acid (*v.* Silbermann and Ozorovitz, Chem. Zentr. 1908, ii. 1024). Derivatives of gallic acid (*v.* Power and Shedden, Chem. Soc. Trans. 1902, 73).

Basic bismuth gallate (*Dermatol*)

$$C_7H_5O_5Bi,2H_2O$$

is prepared from bismuth hydroxide and gallic acid, or from bismuth nitrate and gallic acid in the presence of potassium nitrate and acetic acid. It is a yellow powder, but is obtained crystalline by the second method given above (Thibault, J. Pharm. 14, [vi.] 487; 25, [vii.] 268; May, Amer. J. Pharm. 80, 208; Causse, Compt. rend. 117, 232; Fischer and Grützner, Arch. Pharm. 231, 680). *Bismuthhydroxyiodogallate* (*Airol*) is a greenish-grey powder (Haegler, Chem. Zentr. 1896, i. 764; Torelli, *ibid.* 1898, i. 857; Hoffmann, Traub & Co., Ger. Pat. 80399, 82593; Frdl. iv. 1122, 1123). Both compounds are inodorous antiseptics, and may be used as substitutes for iodoform.

Methyl ester $(HO)_3C_6H_2{\cdot}CO_2CH_3$. Prepared by dissolving gallic acid in hot methyl alcohol, and treating the solution with hydrogen chloride. The alcohol is distilled off, the residue dried and recrystallised from hot water (Kern, Eng. Pat. 5953; Ger. Pat. 45786; Frdl. ii. 167; Hamburg, Monatsh. 19, 594); m.p. (anhydrous from methyl alcohol) 202°; from hot water, crystals contain water of crystallisation, which is driven off at 100°–110°.

Detection and Estimation.—Gallic acid gives a bluish-black precipitate with ferric chloride, but does not precipitate gelatin. On adding 1 c.c. of (1 : 30) potassium cyanide solution to a 1 p.c. solution of gallic acid and agitating, a ruby-red colour is produced, which disappears on standing, but is regenerated by agitation. Pyrogallol and tannic acid give yellowish-red solutions (Griggi, Boll. Chim. Farm. 38 5). Boettinger (Annalen, 256, 341; J. Soc. Chem. Ind. 1900, 450) heats gallic acid with double its weight of phenylhydrazine to 100°, boils the solution for a few seconds, and then lets one drop fall into a beaker containing water made alkaline with caustic soda, when an orange or golden-yellow coloration is produced. Tannic acid gives a blue coloration changing to yellow. In estimating gallic acid in tannins, it is always necessary to separate it from the tannic acid, which is also present (Spica, Gazz. chim. ital. 31, ii. 201; Harnack, Arch. Pharm. 234, 537; Buchner, Annalen, 53, 537; Hinsdale, Chem. News, 64, 51; Dreaper, J. Soc. Chem. Ind. 1893, 412; Chem. News, 90, 111; Proctor and Bennett, J. Soc. Chem. Ind. 1906, 251; Jean, *ibid.* 1900, 382).

GALLIPEÏNE *v* CUSPARIA BARK.

GALLISIN (iso-**MALTOSE**) *v.* CARBOHYDRATES.

GALLIUM. Ga. At.wt. 69·9 (Boisbaudran); 70·1 (Richards, Craig, and Sameshima). Is very widely distributed in nature, although always occurring in minute quantities. It is found in various clay ironstones, in hæmatites, in various aluminous and manganese minerals and ores, in some meteorites and meteoric iron, in zincblendes, pyrites, &c. (Hartley and Ramage, Chem. Soc. Trans. 1897, 533). Perhaps the richest source of this metal is the Middlesborough blast furnace metal obtained from the Cleveland clay ironstone, the cast iron containing 1 part of gallium per 33,000 parts of iron. Gallium belongs to the aluminium group of elements, and is occasionally to be detected in commercial aluminium; it is the eka-aluminium predicted by Mendeléeff, and was discovered by Boisbaudran, in 1875, by means of spectroscopic analysis, in the zincblende of Pierrefitte in the Pyrenees (Compt. rend. 1892, 114, 815).

For its electrolytic deposition and purification, *see* Uhler and Browning, Amer. J. Sci. 1916, [iv.] 42, 389; Richards and Boyer, Nat. Acad. Sci. Proc. 1918, 4, 388; J. Amer. Chem. Soc. 1920, 43, 274. For its qualitative separation and detection, *v.* Browning and Porter, Amer. J. Sci. 1917, 44, 221; J. Amer. Chem. Soc. 1921, 43, 126.

Gallium is a bluish-white, hard, tough, slightly malleable diamagnetic metal; sp.gr. 5·9, sp.ht. 0·080 and of higher sp. resistance than the alkali metals. It fuses at 29·76°, forming a silver-white liquid of sp.gr. 6·096, resolidifying very slowly even at 0°. If, however, a fragment of solid gallium is introduced, it solidifies rapidly in pyramidal monoclinic crystals, and expands on freezing. The expansion on solidification is 0·00531 c.c. per gram. The compressibility of the solid metal is $2·09 \times 10^{-6}$. Liquid Ga has a compressibility of $3·97 \times 10^{-6}$ at 30°. The molten metal, if poured on to a glass, covers the surface with a bright mirror like deposit. The metal is non-volatile at a red heat, is slowly and superficially tarnished in air or water. It is attacked by the halogens, and dissolves in hydrochloric acid and in potash solution with evolution of hydrogen. In nitric acid, it dissolves on warming, with evolution of oxides of nitrogen. It forms liquid alloys with aluminium and indium.

Compounds. *Gallium oxide* Ga_2O_3 is a white powder reduced by hydrogen at a bright red heat, and, according to Winkler (Ber. 1890, 23, 788), also by magnesium: the *hydroxide* is insoluble in water, but soluble in alkalis. *Chlorides*, $GaCl_2$, $GaCl_3$, an *oxychloride*, *bromides*, *iodides*, *sulphates*, *sulphides*, a *nitrate*, a series of *alums* $Ga_2(SO_4)_3·(M)_2SO_4,24H_2O$, and a *silicotungstate* have been prepared (Dupré, Compt. rend. 1878, 86, 720; Boisbaudran, Ann. Chim. 1877, [5] 10, 126; Wyrouboff, Bull. Soc. franc. Min. 1896, 19, 240). Gallium chloride sublimes at a comparatively low temperature, and may thus be separated from less volatile chlorides.

GALLOCYANINE *v.* OXAZINE COLOURING MATTERS.

GALLOFLAVIN. This dye, which can be fixed on mordanted fibres like alizarin, is obtained by the action of air, *i.e.* oxygen, on alkaline solutions of gallic acid. The process of oxidation depends on the amount of alkali present. In practice, 5 parts of gallic acid are dissolved in 80 parts of alcohol of 96°Tw. and 100 parts of water. The cooled solution is gradually mixed with 17 parts of caustic potash solution of 30°B., stirring all the while, and never allowing the temperature to rise above 10°. It is then exposed to the action of oxygen, either by blowing air through it or by agitating it briskly. The progress of the oxidation shows itself by the liquor assuming at first an olive-green or greenish-brown colour, until finally a crystalline precipitate separates out. When the amount of this precipitate no longer increases, the operation is finished. The mass of crystals is quickly filtered, dissolved in warm water, decomposed with hydrochloric or sulphuric acid, and boiled when the dye is precipitated in the state of glistening greenish-yellow plates. These are washed, and can then be applied for dyeing or printing.

Galloflavin dyes cotton mordanted with alumina greenish-yellow, which turns into a very brilliant yellow by treatment with tin crystals. Wool, mordanted with bichrome, is dyed olive-yellow, copper as mordant gives a dark-brown, and stannous mordant dull-orange. In practice, only chrome mordants are used, and the shades obtained are fairly fast to light, soap, and milling, fast to dilute acids and alkalis, but do not compare favourably with the alizarins. The colour is somewhat sensitive to chlorine.

The formula $C_{13}H_6O_9$ was first suggested for galloflavin (Bohn and Graebe), and subsequently $C_{12}H_6O_8$ (Herzig). The substance crystallises in greenish-yellow leaflets, is sparingly soluble in water, alcohol, and ether, more readily soluble in glacial acetic acid and aniline. The *potassium salt* $C_{13}H_4O_9K_2$ (B. & G.) is a crystalline body which is insoluble in alcohol and cold water. The *acetyl derivative*

$$C_{13}H_2O_5(O·COCH_3)_4$$

(B. & G.) or $C_{12}H_2O_4(O·COCH_3)_4$ (H.) crystallises from benzene or ethyl acetate in white needles, m.p. 230° (B. & G.), 230°–233° (H.); is freely soluble in glacial acetic acid and chloroform, but does not dissolve readily in alcohol or ether. The *chloracetyl derivative* $C_{13}H_2O_5(O·COCH_2Cl)_4$ (B. & G.), is very little soluble in alcohol, ether, chloroform, or benzene, easily soluble in acetic acid, and crystallises in needles; m.p. 210°–212°. Galloflavin, on methylation, yields *tetramethoxygalloflavin* $C_{12}H_2O_4(OCH_3)_4$ (H.), crystallising in felted, almost colourless needles from acetic acid; m.p. 236°–239°. When this compound is quickly boiled with aqueous potash, and then treated with strong hydrochloric acid, it yields a crystalline substance, *trimethylisogalloflavin*,

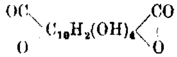
$C_{11}H_2O_3(OCH_3)_3COOH$ (H.), difficultly soluble in alcohol, and crystallising therefrom in fine white needles, melting at 253°–256°, with strong gas evolution. On methylation or esterification, this yields *tetramethylisogalloflavin*

$$C_{11}H_2O_3(OCH_3)_3COOCH_3$$

(H.), crystallising from alcohol in long needles; m.p. 232°–234°. Heated under reduced pressure, trimethyl*iso*galloflavin loses carbon dioxide, and *a substance*, $C_{11}H_3O_3(OCH_3)_3$ (H.), distils over at 270°–300° (28 mm. pressure), which sets to a yellowish-white crystalline mass, is difficultly soluble in alcohol, and can be crystallised therefrom in white crystals; m.p. 130°–134°. On methylating trimethyl*iso*galloflavin with aqueous alcoholic potash and methyl sulphate, and finally with diazomethane, there is obtained *a substance*, $C_{10}H_2O(OCH_3)_4(COOCH_3)_2$ (H.), crystallising out of methyl alcohol and melting at 92°–95°. This substance is easily hydrolysed to the corresponding *dibasic acid*

$$C_{10}H_2O(OCH_3)_4(COOH)_2$$

(H.), crystallising from dilute methyl alcohol, and melting at 214°–215° with gas evolution. This dibasic acid, on heating under reduced pressure, loses carbon dioxide, and *a monobasic acid* $C_{10}H_3O(OCH_3)_4COOH$ (H.) distils over at 260°–280° (28 mm. pressure), which sets to a solid, and, crystallised from ethyl acetate, melts at 132°–135°. This series of transformations from tetramethylgalloflavin indicates that it probably contains two lactone bonds, and that galloflavin itself may be represented as:



$$\begin{array}{ccc} OC & & CO \\ & \diagdown C_{10}H_2(OH)_4 \diagup & \\ O & & O \end{array}$$

References.—Ger. Pat. 37934, 1886; Frdl. i. 567; Knecht, Rawson, and Loewenthal, Manual of Dyeing; Bohn and Graebe, Ber. 20, 2328; Herzig and Tscherne, Monatsh. 25, 003; Herzig, Sitzungsberichte der K. Akademie der Wissenschaften in Wien. Math-naturw. klasse Bd. 119, abt. ii. *b*, Juni, 1910.

GALLOGEN, GALLOL *v.* SYNTHETIC DRUGS.

GALLOTANNIC ACID *v.* *Digallic acid*, art. TANNINS.

GALVANISED IRON *v.* ZINC.

GALYL. A derivative of salvarsan. 4 : 4′-Dehydroxyarsenobenzene-3 : 3′-phosphamic acid. Used in the treatment of syphilis and other protozoal diseases (*v.* ARSENIC, ORGANIC COMPOUNDS OF).

GAMBINE. *Nitroso-β-naphthol* (*v.* QUINONE-OXIME DYES).

GAMBIR or **GAMBIER.** The Malayan name of an extract obtained from the *Uncaria Gambier* (Roxb.). It is the *Terra japonica* of tanners (*see* CATECHU).

GAMBOGE *v.* GUM RESINS.

GAMMA (γ) **ACID.** 2-Amino-8-naphthol-6-sulphonic acid.

GAMMAM. A Tunisian dyestuff of unknown origin.

GANISTER. A local name of unknown origin for a hard siliceous sandstone occurring in the coal-measures of the north of England. Formerly it was employed as a road-stone, but now it is much used for making refractory ganister- or silica-bricks and for the linings of steel furnaces and converters. The name has been also loosely applied to other siliceous materials used for making fire-bricks. In the typical locality, namely in the neighbourhood of Sheffield, the rock occurs beneath thin seams of coal at a definite horizon—the Ganister group—in the lower coal-measures. The best bed, lying immediately beneath the Hard Mine coal, varies in thickness from a few inches to 5½ feet, with an average of 2½ feet. Here it is a hard compact rock with a very fine and even-grained texture, and consists of sub-angular grains of quartz, mostly 0·15–0·5 mm. across, closely packed together and cemented with secondary silica. No appreciable amounts of mica, felspar, or carbonates are present. The rock thus has the character of a quartzite. It is light to dark grey in colour, and is often iron-stained along the joint surfaces. It breaks with a splintery to sub-conchoidal fracture with sharp edges. Carbonaceous patches and streaks, and fossil tree-roots are embedded in the rock. It consists of 90–95 p.c. of silica with small amounts of alumina, iron oxides, lime, and alkalis. Sp.gr. 2·59. Silica rocks of very much the same nature are widely distributed in most of the coal-fields of England, Wales, and Scotland; *e.g.* the Dinas rock (or 'clay') from the Vale of Neath in Glamorganshire, which contains as much as 98 p.c. of silica. They pass insensibly, both laterally and vertically, into siliceous fire-clays ('bastard ganister'). The rock is won by quarrying or underground mining, and is crushed, ground, and mixed with lime (1–1½ p.c.) or fire-clay to act as a binder. This mixture is moulded into bricks, which, after drying, are fired at about 1500°, or it is applied directly as a furnace lining, or used for setting the bricks and patching and repairing furnaces. Ganister is also ground to a fine sand for use in casting iron and brass (*v.* Mineral Resources of Great Britain, Mem. Geol. Survey, 1918, vol. vi. (2nd edit., 1920); and 1920, vol. xvi.; A. B. Searle, Refractory Materials, London, 1917). L. J. S.

GARANCEUX and **GARANCINE** *v.* MADDER.

GARBAGE FATS. Under the name 'garbage fats' may be comprised all those fats contained in house and other refuse which do not find their way into the sewers. Such refuse is generally collected by the municipalities and destroyed as soon as possible, the primary object being to remove it rapidly from inhabited areas and dispose of it in a sanitary, or at any rate in the least objectionable, manner. The system in vogue in this country, and rapidly superseding the older method of dumping on waste land, is to destroy the refuse in specially designed destructors, after a rough sorting out of tins, iron pots, old leather, &c., has taken place in the destructor works. Thus all putrescible matter, together with the fat present, is destroyed. Hence efforts have not been wanting to recover the fatty matter. In the United States of America especially methods for the disposal of garbage have been developed. An early process (worked in Buffalo about 1885) consisted in extracting the garbage with light petroleum. This has, however, been superseded by cheaper processes comprised under the term 'reduction processes.' These processes are very similar to the methods used in the rendering of fish oils (*see* MENHADEN OIL), and slaughter-house greases.

In several cities of America, the Arnold-Egerton process is worked, in which the fatty matter is extracted by purely mechanical means. The garbage is delivered into large digestors, in which the mass is boiled with steam. After boiling at 80 lbs. pressure, the whole mass collects into three layers, the top layer of which forms the separated grease. This grease is sold for the manufacture of low-class soaps and low-class lubricants. It has a dark-brown colour, and is characterised by a large amount of free fatty acids and unsaponifiable matter. Not infrequently it develops an unpleasant odour when kept. J. L.

GARCINIA INDICA (Choisy). A plant belonging to the order *Guttiferæ*. The pericarp of the fruit is used at Goa as a spice, and the blood-red acid juice as a lemonade. The seeds yield 30 p.c. of fat, which contains 50 p.c. of stearic acid. The cake left after the removal of the fat contains a fine red colouring matter soluble in water and alcohol (Bouis and Pimentel, Compt. rend. 44, 1355).

GARDENIA GRANDIFLORA. The fruit of the *Gardenia grandiflora*, known as 'Wongsky,' is or was employed in China for dyeing yellow, as an assistant for the production of green colours, and in conjunction with safflower. According to Crookes (Dyeing and Calico Printing, 422), it has not been much used in this country, and the yellow and orange colours it yields are of a somewhat fugitive character.

Rochleder and Mayer (J. pr. Chem. 74, 1) isolated from it pectin, the rubichloric acid (chlorogenin) which is present in Madder, Chay-root and Morinda root (*l.c.*), tannin, and a red amorphous colouring matter apparently identical with the crocin of saffron (*Crocus sativus*). Persoz obtained the colouring matter as a reddish crystalline mass (Crookes, *l.c.*), and found that this dyed cotton when mordanted with alumina, yellow, and when mordanted with iron an olive colour.

In Bancroft's Philosophy of Permanent Colours, i. p. 285, mention is made of the use of the *Gardenia florida* by the Chinese for the dyeing of scarlet under the name of 'unki.'

The Decamalee or Dikamali gum, which is obtained in India from the *Gardenia lucida*, contains, according to Stenhouse and Groves (Annalen, 200, 311), *gardenin* $C_{14}H_{12}O_6$, m.p. 163°–164°, and this was isolated as deep yellow crystals insoluble in water and alkaline solutions. A. G. P.

GARLIC. *Allium sativum* var. *vulgare* (Döll.). A plant extensively used as a condiment in Spain, Portugal, Northern Africa, and other countries.

König gives as its average composition—

Water	Protein	Fat	Carbohydrates	Fibre	Ash
64·6	6·8	0·1	26·3	0·8	1·4

Among the carbohydrates is included 0·9 p.c. of pentosans. The characteristic odour and flavour of garlic are due to an essential oil, amounting to about 0·2 p.c. of the weight, which consists mainly of allyl sulphide and allyl isothiocyanate, the former largely predominating. A wild species, *Allium vineale*, is a troublesome weed in pastures and meadows, and when eaten by dairy cows imparts its disagreeable flavour to the milk. H. I.

GARNET (Ger. *Granat*; Fr. *Grenat*). A group of minerals differing widely in chemical composition, but all conforming to the general orthosilicate formula $R_3''R_2'''(SiO_4)_3$, where R''=Ca, Fe, Mg, Mn; and R'''=Al, Fe, Cr, or rarely Ti. The following principal types may be distinguished:—

Calcium-iron-garnet	$Ca_3Fe_2Si_3O_{12}$	Andradite
Calcium-chromium-garnet	$Ca_3Cr_2Si_3O_{12}$	Uvarovite
Calcium-aluminium-garnet	$Ca_3Al_2Si_3O_{12}$	Grossularite
Iron-aluminium-garnet	$Fe_3Al_2Si_3O_{12}$	Almandine
Magnesium-aluminium-garnet	$Mg_3Al_2Si_3O_{12}$	Pyrope
Manganese-aluminium-garnet	$Mn_3Al_2Si_3O_{12}$	Spessartite

Only exceptionally is the composition of actual garnet crystals as represented above. As a rule, several, or even all, of these compounds enter into isomorphous mixtures; and whilst there is generally a preponderance of one or other of them, this is not always the case. All the members of the group crystallise in the cubic system, usually with the form of the rhombic-dodecahedron or the icositetrahedron, or a combination of these. The crystals are often rounded or granular in form. There is no cleavage, and the lustre often inclines to resinous in character. Corresponding with the wide range in chemical composition, these minerals exhibit a wide range in colour (yellow, brown, red, green, black, rarely colourless, but not blue), transparency, sp.gr. (3·15 to 4·3), hardness (6½–7½), and mode of occurrence. They occur as primary constituents of igneous rocks; in gneisses, schists, and crystalline limestones; in veins and encrusting the walls of crevices in rocks. Granular rocks composed wholly of garnet are also known.

The chief application of garnet is as a gem-stone, of which there are several beautiful varieties. *Hessonite*, or cinnamon-stone, is a variety of calcium-aluminium-garnet, containing small amounts of ferrous and manganous oxides; its colour is a warm yellowish-red. *Almandine* is deep red, often with a violet tinge. *Pyrope* (Bohemian garnet, 'Cape ruby') is a fiery red. *Rhodolite*, a variety midway between almandine and pyrope in composition, is remarkable for its delicate rhododendron-red colour. *Demantoid* is a calcium-iron-garnet of a rich emerald-green colour and with a brilliant lustre.

Garnet is also used as an abrasive agent, mainly in the form of sand, for sawing and grinding stone and for making garnet-paper (often sold as 'emery-paper'). Owing, however, to its lower degree of hardness, it is of less value than corundum and emery. Practically the whole of the massive garnet used for this purpose is mined in the eastern United States, principally New York, but also Connecticut, Pennsylvania, and North Carolina. The output amounts to about 5000 tons per annum, valued at about 6*l.* per ton. In the garnet-mining district of the Mittlegebirge in northern Bohemia, the small material, left after picking out the stones suitable for cutting as gems, is used for gravelling garden walks. L. J. S.

GARNIERITE. A hydrated silicate of magnesium and nickel, of importance as an ore of nickel. It is soft and earthy, greasy to the touch, and usually of a bright apple-green colour; sp.gr. 2·3–2·8. The composition is variable (SiO_2, 35–52; MgO, 2–37; NiO, 2–50; H_2O, 10–20 p.c.), and the material is probably a mixture. It may be regarded as a hydrated magnesium silicate, allied to serpentine, in which variable proportions of magnesium are replaced by nickel. The darker green varieties are sometimes distinguished by the name *noumeite* (from Noumea in New Caledonia), the name garnierite (after Jules Garnier, the discoverer of the New Caledonian nickel ores) being reserved for the lighter-coloured varieties. A chocolate-coloured variety, containing iron, has been called *chocolite* (J. Garland, Nickel Mining in New Caledonia, Trans. Inst. Mining and Metall. 1894, 2, 128, 224). *Nepouite*, from Nepoui, New Caledonia (E. Glasser, Compt. rend. 1906, 143, 1173), is a finely crystalline variety for which the formula is given as $3(Ni,Mg)O{\cdot}2SiO_2,2H_2O$, the amount of nickel oxide ranging from 18 to 50 p.c.

These minerals occur in veins traversing serpentine rocks in the neighbourhood of Noumea, or Numea, the capital of New Caledonia; and, like the serpentine, they have been produced by the alteration of peridotite rocks, the olivine of which contains traces of nickel. Over 100,000 tons of these nickel ores are exported annually from New Caledonia.

Large deposits, forming beds 10 metres in thickness, of the same type of ores occur, also in connection with serpentines and olivine rocks, at Riddles, in Douglas Co., Oregon. The nickel mineral from this locality is sometimes referred to *genthite*, $2NiO{\cdot}2MgO{\cdot}3SiO_2,6H_2O$. Other similar occurrences are met with and to some extent mined at Webster in North Carolina, at Texas in Lancaster Co., Pennsylvania (genthite), at Revda in the Urals (revdanskite), and near Frankenstein in Prussian Silesia (pimelite, alipite, &c.).

On the New Caledonian ores, *see* A. Liversidge, The Minerals of New South Wales, &c., 1888, 275; F. D. Power, Trans. Inst. Mining and Metall. 1900, vol. 8, 426, with bibliography; E. Glasser, Ann. des Mines, Paris, 1903, ser. x. vol. 4, 363. L. J. S.

GAS, AIR. When a current of air is passed over or through a volatile liquid hydrocarbon, such as petrol, gasolene, or benzene, the air becomes charged with a certain amount of the vapour from the hydrocarbon and is rendered inflammable, the mixture being known under the name of 'air gas.' Of the various hydrocarbons that have been tried, petrol has proved to be the most useful, on account of its extreme volatility and freedom from impurities which have a slower rate of evaporation.

Petrol is the first distillate from the crude oil as it comes from the oil well, and consists largely of pentane C_5H_{12}, hexane C_6H_{14}, and heptane C_7H_{16}, the first liquid members of the great paraffin group of hydrocarbons. It is volatile, and has a flash-point below the freezing-point of water: one gallon of petrol, on being vaporised, will give 28·4 cubic feet of vapour, whilst a pint of it poured on a level surface will cover about 80 square feet with an inflammable vapour, through which, on coming in contact with a light, a flame will spread; and 100 cubic feet of air can be made highly explosive by the vapour from a pint of petrol.

Attempts to produce an illuminating gas by carburetting air with the vapour of some volatile hydrocarbon, date back to 1841, and until 1889 the mixture was made rich enough to produce a luminous flame. This meant that a large percentage of vapour was required, but on this account, and also by reason of the varying quality of the hydrocarbon employed, as well as the inefficiency of the carburettors, it proved very difficult to maintain the production of a gas of uniform composition, with the result that the amount of light obtained at the burners fluctuated. Owing to these drawbacks, the development of lighting by means of carburetted air remained in abeyance until the introduction of petrol of fairly uniform composition for motor-cars and the extended use of the incandescent mantle turned the attention of inventors once more to the possibilities of the process.

Using an incandescent mantle, there is no need for a rich gas, so that the proportion of hydrocarbon vapour can be reduced to a considerable extent, thus doing away with many of the troubles attending the carburation of the air.

If air be passed over or through a vessel containing petrol, the resulting mixture is of very uncertain composition, as at the commencement the more volatile constituents evaporate very quickly, yielding a gas which is far too rich, whilst at the end of the operation, owing to the loss of these lighter portions, the residue does not evaporate at anything like the same rate, so that the air cannot take up the requisite amount of vapour, and the gas is of poor quality. Moreover, when evaporation takes place, a certain amount of heat is absorbed or rendered latent, which reduces the temperature of the petrol in the carburettor, and as the temperature falls, so it evaporates less readily, thus affecting the composition of the mixture. It is essential, for obvious reasons, that a gas supply, whether for heating, lighting, or power purposes, should be as constant in quality as possible, and this has led to the introduction of a host of devices, the aim of which is to secure a gas of definite and uniform composition.

In the majority of air-gas generators in use at the present time, the incandescent mantle is employed to develop light from a mixture of petrol vapour and air so poor in hydrocarbon that it gives a non-luminous but sufficiently hot flame to raise the mantle to incandescence.

When petrol vapour is added little by little to air, it is found that with 1·2 p.c. of vapour, a flame will just travel through the mixture; with 1·5 p.c., the mixture burns under proper conditions; whilst with 2 p.c., the mixture becomes explosive, increases in explosive force up to 2·6 p.c., and gradually diminishes in explosibility until 5 p.c. of the vapour is present, when it becomes non-explosive and burns quietly once more.

It is clear, therefore, that if a mixture of from 1·5 to 1·8 p.c. of petrol vapour with air can be made, such a gas will burn with a non-luminous flame in a properly constructed burner without the addition of more air, and which will have sufficient flame temperature for use with a mantle, whilst it has the enormous advantage that, if through a leak it should escape into the air, the admixture of more air with it renders it non-explosive instead of, as in the case of ordinary coal gas, giving an explosive mixture.

This property was first utilised by Hooker in his safety air gas, and has been the objective of all air-gas apparatus makers since his time, as it enables something like 1400 to 1500 cubic feet of air gas to be made from a gallon of petrol, and yields most economical results, as in properly constructed burners such gas will give about 9 candles per cubic foot consumed with an incandescent mantle.

Combustion, with the better qualities of petrol, is represented by the following equation:—

$$2C_6H_{14}+19O_2=12CO_2+14H_2O$$

At the present time, air-gas apparatus may be divided into two classes:

(1) Those which give an air gas containing over 5 p.c. of the hydrocarbon vapour, and therefore require the addition of air in a Bunsen burner before combustion in the mantle; and

(2) Those in which the percentage of hydrocarbon vapour is under 2 p.c., and the gas is burnt in burners of proper construction without the addition of more air.

To the first class belong such forms of apparatus as the 'Aërogen,' in which the gas is afterwards burnt with a further addition of air. Such forms of apparatus have been in use on the Continent for many years, in some cases being utilised for the lighting of large villages from a central supply station. To the second class belong by far the largest number of generators, such as those which have from time to time made their appearance under such names as the 'Non-explosive Gas,' the 'Praed,' the 'Eos,' the 'Safety Light,' the 'National,' the 'Globe,' the 'Loco,' 'Solux,' 'Centenary,' and several other systems.

In all these forms of machine, the apparatus is designed automatically to mix or evaporate the petrol with air in the right proportion, no matter whether it supplies a large or small number of lights, and in order to do this it is useless to employ carburettors in which a current of air flows over the surface of or through the petrol, and the best results are obtained by introducing small quantities of petrol into a carburettor of suitable form, where it meets with exactly the amount of air necessary to vaporise it entirely, producing the gas of the required composition. This is done in several ways. In one type of apparatus, a current of air is forced by a fan driven from a hot-air engine through the carburettor, where it meets with the supply of petrol, which is pumped up from a storage tank below the apparatus, and entering the carburettor at the top in the right ratio to the air supply is injected into the current of air as a spray, thus ensuring immediate volatilisation.

In another type of machine, the flow of petrol to the carburettor is regulated by a mercury valve contained in a chamber outside the carburettor. As the level of the petrol in the carburettor sinks, so the mercury seal is opened, allowing more petrol to flow into the carburettor in just sufficient quantity to replace the loss. In a third system, the air is forced in through a rotating meter, the revolving spindle of which works the regulator of the petrol tank. In the carburettor, the petrol flows on to the surface of a sphere or ball, round which the air is made to circulate in such a way as to completely evaporate all the petrol, the mixture being, at the same time, well agitated by a fan to ensure thorough mixation and uniformity of composition.

Another form of apparatus consists of a multi-chambered turbine arrangement. The petrol and air in definite quantities are admitted into each chamber in succession, and violently agitated therein, with the result that the petrol is almost instantly vaporised, the carburetted air being discharged into a central mixing chamber into which the gas from each chamber flows before it passes off to the holder.

The motive power for the production of the necessary pressure of air can be obtained by the slow descent of a weight, by water power, or, most generally, by a hot-air engine actuated by the combustion of a small portion of the air gas itself.

The drawback to the use of a falling weight is that, unless an abnormal length of fall be arranged for, its period of working is comparatively short before it requires winding up again. Water is reliable, and serves well where a supply is available, but the cost is high if it has to be paid for. The hot-air engine as now made consumes but a very small amount of gas, and is of simple yet reliable construction: it runs noiselessly, and can keep at work for indefinite periods with the minimum of attention.

The burners employed for the combustion of the air gas naturally vary with the quality of gas made, as with gas containing below 2 p.c. of vapour no admission of air before combustion is needed, and the burners have to be packed with small tubes or wire gauze, so that if by any chance an explosive mixture is formed in the generator, owing to the amount of petrol vapour having risen to over 2 p.c., flashing back to the regulating apparatus, and so causing an explosion, would be prevented: with those machines which give a mixture richer than 5 p.c. in vapour, a burner of the ordinary Bunsen type, capable of very delicate adjustment, has to be employed, but in no case must an apparatus be installed in which there is no arrangement, such as a safety chamber, between the burners and the regulating drum for the prevention of a flash-back.

With regard to the installation and distribution of the gas, owing to its sensitiveness to atmospheric conditions, great attention should be paid to the arrangement of the falls in the pipes, and siphons should be inserted where there is any chance of a deposit accumulating. It must be mentioned that the chief drawback to petrol-air gas is the very heavy condensation which occurs in the distributing pipes, and in a few instances, where prevailing conditions are amenable to the deposition of moisture, the system has had to be abandoned almost entirely owing to the trouble arising from this cause. This is particularly the case when plants are employed in which heat is employed for effecting vaporisation. It is an advantage to use pipes of rather larger diameter than would be adopted for coal-gas lighting, especially for installations producing a weak gas, as the volume of gas consumed per candle power is more than double that of coal gas, but existing pipes can be utilised in many cases, providing they are not less than ¾ inch in bore. As regards the fittings, the ordinary coal-gas fittings can generally be employed, provided the gas way is of sufficient size to be consistent with the extra volume of gas consumed.

The heating power of air gas is of course dependent upon the percentage of petrol vapour which it contains, and as the different commercial makes of petrol, benzene, &c., which could be employed in such plants vary, it is necessary to know not only the percentage of petrol vapour present, but the source of such vapour. Whereas for lighting alone a gas of low calorific power may be employed, for such purposes as cooking and heating the mixture should be of about 6 p.c. saturation when a gas of about 300 B.Th.U. will be obtained.

The calorific power of standard grades of spirit employed in air-gas machines and internal combustion engines varies between 130,000 and 135,000 B.Th.U. per gallon, density at 15° ranging between 0·68 and 0·72.

The enormous increase in the cost of petrol occasioned by the European war reacted very much to the disadvantage of air gas, for, on the basis that 1 gallon of spirit yields 5000 candle-power hours, the candle hours obtained for 1*d.* amount to only 120 with petrol at 3*s.* 6*d.* per gallon. In contrast to this, it may be mentioned that ordinary coal gas at a price of 3*s.* 6*d.* per 1000 cubic feet yields in the low-pressure inverted incandescent burner so much as 480 candle hours.

V. B. L.

GAS CARBON *v.* CARBON; also GAS, COAL.

GAS, COAL. During the 17th and 18th centuries, several observers noticed the evolution in the neighbourhood of coal-fields of combustible gas, which burned with a luminous flame, and also that a gas of this nature was produced by the distillation of coal in closed vessels, but the first to carry out the process of the distillation of coal for the special purpose of producing a gas for use as an illuminant was William Murdoch, who, in 1792, lighted his house at Redruth by this means. At that time, Murdoch was in charge of James Watt's condensing steam engines recently erected at Cornish mines by Messrs. Boulton and Watt, of which firm he was the representative, and on returning later to the works of Messrs. Boulton and Watt at Soho, Birmingham, he continued his work on the subject, and, probably in 1798, lighted a part of the works with coal gas. Independently of Murdoch, but at a rather later date, Philippe Lebon of Paris also employed for lighting purposes the gas evolved by the distillation of wood, the date of his first patent being 1799.

From 1803 onwards, installations of coal-gas plant were introduced for lighting various houses and factories, largely by Murdoch and Boulton and Watt, but they do not appear to have contemplated the erection of works for a public supply of the gas, although this plan had been advocated already by Lebon. F. A. Winsor or Winzer, a native of Moravia, had become acquainted with Lebon's ideas when in Paris, and on settling later in London, he commenced an agitation for the foundation of a company there for the manufacture and supply of coal gas, and marred though his efforts were by gross extravagance of statement and unjustifiable claims, they were nevertheless eventually successful in 1810 in obtaining an Act of Parliament for the formation of a Statutory Company in London, which two years later received a charter of incorporation, and still continues under the name of the Gas Light and Coke Co., London.[1]

From this time forward, the manufacture and public supply of coal gas has steadily increased, but until the last quarter of the 19th century, the coal gas was almost exclusively employed for illuminating purposes, by utilising the luminosity developed by burning it in open flames, and the quality of chief importance was its illuminating power. During the last 40 years, however, the conditions have completely altered, owing to steadily increasing employment of the gas for the purposes of heating and cooking, and for the production of power by its use in gas engines, for which purposes the calorific power of the gas is the chief factor of importance. Moreover, since the introduction of the incandescent burner by Auer von Welsbach in 1887, this method of lighting, in which a mantle composed of thoria and ceria is heated to incandescence by a Bunsen flame, has, to a very great extent, replaced the open flame burners, the number of which is still steadily decreasing, probably less than 5 p.c. of the gas supplied being now thus used. With the incandescent burner, the light evolved is dependent mainly, though not entirely, on the calorific power of the gas, but has no direct connection with its illuminating power when burnt in open flames, so that at the present time, so far as the great bulk of the gas supplied is concerned, its calorific power is the property of primary importance.

During the last 50 years, great progress has also been made in the manufacture of gas having low illuminating power, and containing a large proportion of inert gases such as nitrogen and carbon dioxide, but which can be produced at a low price and has still sufficient calorific power for employment in gas engines and for furnace heating, and such gas is now also produced in very large quantities, being, in most cases, manufactured at the works where it is required, and not distributed from a central station (*see* FUEL). Here, however, only the production of what is ordinarily known as 'coal gas' will be considered, that is, the gas distributed for public use and capable of being employed at the desire of the consumer for lighting, heating, or power purposes. The magnitude and extent of this industry and the manner in which it has extended during 34 years is shown in the table (p. 307), giving the summary of the figures in the Board of Trade returns from all authorised gas undertakings belonging to 816 statutory gas companies or local authorities for the years 1885, 1909, 1913, and 1919.

This table does not include the production of private companies, but their total output is very small, and would not materially affect the figures. The total amount of coal carbonised by these small private undertakings, some 800 in number, is not more than 500,000 tons annually.

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[1] For a full account of the early history, see *A History of the Introduction of Gas Lighting*, by C. Hunt (Walter King).

—	Capital or loan authorised	Paid up and borrowed	Tons of coal carbonised	Number of cubic feet of gas made	Number of cubic feet of gas sold	Length of gas mains in miles	Number of consumers	Number of public lamps lighted
	£	£		thousands	thousands			
1885 .	71,863,267	35,513,570	8,378,904	84,637,727	77,393,670	18,967	2,095,025	402,074
1909 .	154,500,093	132,123,284	15,225,320	193,547,394	177,686,943	35,230	6,164,066	712,903
1913 .	163,346,673	139,727,277	16,971,724	224,517,167	206,474,473	39,079	7,103,113	741,703
1919 .	176,353,107	149,978,436	19,033,712	249,566,414	228,537,998	40.109	7,540,133	545,712

In addition to the gas output, coke, tar, and ammonia are also produced in large quantities as by-products. The exact figures for coke and tar are not available, but approximately 7 to 8 million tons of coke and 160,000,000 gallons of tar are now sold annually from gasworks alone. The production of ammonia from gasworks in 1920, calculated as sulphate, was 176,196 tons.

Principles of manufacture. Up to within the last few years, the method of manufacture of coal gas has remained in its general principles almost identical with that employed by Murdoch and his immediate successors (prominent among the latter being Samuel Clegg, senr., and his son, Samuel Clegg, junr.), although in detail and in the magnitude of the operations, great change has taken place. So far as the actual carbonisation of the coal is concerned, Murdoch, after experimenting with different types of retort, settled down to the employment of long, narrow retorts set horizontally, into which the coal was charged all at once in such a manner as to leave a free space above the coal throughout the whole length of the retort, the charge being then allowed to remain in the retort until it was completely carbonised, when the residual coke was raked out and the retort recharged with coal; and this plan is still the one employed in the majority of cases. At first, cast-iron retorts were used, but the rapid wearing out of these, especially when the temperature of carbonisation was increased, soon led to the substitution of fireclay for cast iron, and such fireclay retorts have long been in universal use, except in a few very small works.

The further treatment of the hot volatile products issuing from the retorts to obtain a gas suitable for distribution, still generally follows the lines adopted in the earlier days of the industry. These products are first cooled to approximate atmospheric temperature, when the condensible vapours liquefy, forming tar, and the steam always present in quantity condenses to water, the latter then dissolving part of the ammonia present in the gas as well as other gaseous impurities, especially sulphuretted hydrogen and carbon dioxide. The remainder of the ammonia is removed by washing with water (wet purification). For the further purification of the gas, the latter, after removal of the ammonia, was in the earliest stages of the industry passed through milk of lime, which removes the whole of the sulphuretted hydrogen and carbon dioxide, and some of the carbon disulphide present in small amount, but the use of milk of lime was soon replaced by that of slaked lime in a slightly moist condition (dry purification), placed in layers in a closed purifier constructed in such a manner that the gas filtered through successive layers of this material. At a rather later date, hydrated ferric oxide, placed in similar purifiers, was employed for the removing the sulphuretted hydrogen, the carbon dioxide being then either separately removed by lime or allowed to remain in the gas.

After the coal-gas industry became firmly established, there was, as already stated, for a long time no material alteration in principle in the manufacture, but very considerable changes took place in the details of the plant and in the construction of apparatus of large size to deal with the constantly increasing demand. Until about 1880, gas undertakings were subjected to but little effective competition from other means of producing artificial light, especially in towns, but from that time, competition has steadily increased, on the one hand from the electric light, and on the other from the introduction of cheap mineral burning oils, and the stimulus of effective competition has resulted in a much more rapid advance, both in the technical aspects of the manufacture of the gas and in the commercial methods adopted in its sale.

The technical advances have, until recently, involved no great alteration of principle, and have consisted generally in improving the efficiency and economical working of the plant employed, and in the introduction of mechanical transport for the large quantities of material which have to be dealt with, including the adoption of labour-saving machinery. Further, the temperatures at which the coal is carbonised have been increased, resulting in a larger yield of gas per ton of coal, and although such gas is of lower illuminating and calorific power, the falling off is much less than the increase in yield, especially as regards the now more important quality of calorific power. In consequence of these changes and the increased use of gas for other purposes than that of lighting, which has resulted in a more uniform demand for gas over the 24 hours of the day and in the summer and winter months, the price of gas had, up to the outbreak of war in 1914, on the average, steadily fallen, in spite of the fact that the cost of the raw materials and the rate of labour remuneration had risen considerably.

The actual price varied very much, according to local conditions, such as the magnitude of the works and its distance from suitable coal supplies, and also with the character of the financial and technical administration of the undertaking, both in the present and in the past. Up to the year 1914, the lowest price charged was 1*s.* 2*d.* per 1000 cubic feet for general purposes and 1*s.* per 1000 cubic feet for power purposes, and except in the case of small undertakings at a distance from the coal-fields, the price rarely exceeded 3*s.* 6*d.* per 1000 cubic feet.

Since the year 1914, however, the very

great increase in the cost of coal, plant, materials, and labour has resulted in a corresponding large increase in the cost of gas, and whilst as before the price charged in different parts of the country varies greatly in accordance with local conditions, this now generally amounts to about double the pre-war charge. At the same time a material reduction in the calorific power of the gas has taken place in most cases, partly due to the coal and oil shortage, partly to the difficulty of maintaining the manufacturing plant in efficient repair and of building extensions of plant, and partly owing to the necessity for war purposes of extracting the benzene and toluene content of the gas. Owing to this abnormal state of affairs, the various statutory stipulations as to the calorific or illuminating power of the gas to be supplied by the various gas undertakings were practically suspended during the latter part of the war period. At its conclusion the Fuel Research Board of the Department of Scientific and Industrial Research were asked by the Government to report on the matter of the future control of the industry, and their recommendations, modified in certain details after consideration by the Board of Trade and consultation with the Gas Industry, were made statutory by the Gas Regulation Act of 1920.

By this Act fundamental and far-reaching alterations were made in the conditions under which statutory gas undertakings were to carry on their business. Up to the year 1913, the general principles adopted in the control were as follows: In the case of gas undertakings controlled by Local Authorities, a certain minimum illuminating power was prescribed in the Special Act relating to the undertaking, and, in addition, the maximum price which could be charged per 1000 cubic feet of gas, and the usual clauses with regard to sinking fund for repayment of capital. In the earlier period undertakings owned by companies were treated in a somewhat similar manner, their minimum illuminating power and a maximum price being prescribed, and also a maximum dividend payable. It was also usually provided that any new capital raised by such companies must be sold either by auction or by tender and not issued at its par value. Later the maximum price and maximum dividend clauses were dropped in the case of the majority of the statutory companies, and replaced by the adoption of a "standard price" and "standard dividend," and a sliding scale introduced, whereby for each penny the price of gas was reduced below the standard price, an additional dividend (mostly about ⅛th per cent.) was payable above the standard dividend, and *vice versa*, if the price of gas increased above the standard, a similar amount had to be deducted from the dividend payable. Those sliding-scale clauses, which made it to the interest of the gas companies to reduce the price to its lowest possible figure, had given general satisfaction up to the outbreak of war in 1914, but the great increase in costs of coal and other materials so increased the cost of gas above the standard price, that the sliding scale resulted in a very great reduction, and in some cases a disappearance of the dividend payable. As a temporary measure, a short Act was passed in 1917 whereby it was enacted that till the end of the war, the sliding scale clauses should not be operative after they had reduced the dividend payable to two-thirds of the standard dividend.

The actual illuminating power prescribed varied considerably with the different undertakings according to the conditions of coal supply and the character of the demand for gas, and in the years just preceding 1913, a few undertakings had received parliamentary sanction for the substitution of a calorific power standard for an illuminating power standard.

The most fundamental change made by the Gas Regulation Act of 1920, is that of the basis on which the gas is charged for. In place of a charge based on the volume of gas (1000 cubic feet) of a specified illuminating or calorific power the charge will in future be made on the number of British Thermal Units (Gross) contained in the gas supplied, or in other words, on the Potential Energy contained in the gas, and all stipulations as to the illuminating power of the gas in open flame burners are repealed. The unit of measurement is taken as 100,000 British Thermal Units Gross, which is defined by the Act as "a therm."

Each undertaking is left free to "declare" what calorific power of gas per cubic foot it will supply, having regard to its local conditions in respect of coal supplies, manufacturing plant, &c., but it must then maintain such declared calorific power as a minimum, under penalty for failure, or give due notice of such alteration and carry out at its own cost any necessary adjustments of consumers' appliances as may be necessary to enable them to use the gas of altered quality with efficiency. The actual volume of gas supplied to consumers will be determined by meters as at present, and the volume of gas shown, multiplied by the calorific power per cubic foot and divided by 100,000, will give the number of therms on which the charge is to be made at the price determined by the Act or Order of the undertaking concerned.

Further, the Board of Trade are authorised to substitute for the maximum price or standard price per 1000 cubic feet of gas specified in the Acts or Orders of each undertaking, a price per therm as nearly as may be corresponding to the former price per 1000 cubic feet, but "with such addition as appears to the Board reasonably required in order to meet the increases (if any) due to circumstances beyond the control of, or which could not reasonably have been avoided by, the undertakers, which have occurred since June 30th, 1914, in the costs and charges of and incidental to the production and supply of gas by the undertakers."

In addition, the former clause as to the absence of sulphuretted hydrogen from the gas is maintained, and a more stringent stipulation as to the minimum permissible pressure of the gas is made, this not to be less than 2 inches of water in any main or service pipe between the main and the meter exceeding 2 inches in diameter. In view of the difficulties caused by the war in carrying out renewals and extension of manufacturing plant and the distribution system, 5 years are allowed before the above pressure stipulations become fully operative.

The Act also stipulated that the Board of

Trade should as soon as possible cause inquiries to be held into two other matters on which opinion was divided, namely, (1) whether any restriction should be made on the percentage of carbon monoxide supplied in gas used for domestic purposes, and (2) whether there should be any limitation in the percentage of incombustible constituents present in the gas. Committees appointed by the Board of Trade have since reported that no restriction is advisable in respect to carbon monoxide. In respect to incombustible constituents, the committee also report that no restriction is advisable at present, but recommend that the matter should be further considered after a period of a few years when more evidence will be available, owing to gas undertakings having had a period of working under the new conditions resulting from the Act of 1920.

As there are over 800 statutory undertakings, each with its separate Act or Order, a considerable period is necessary for the Board of Trade to effect the revision of these, and although progress has been made, only a minority of the undertakings are yet working under the new conditions. Among those which are, there is a considerable difference in the calorific value "declared" which varies from a maximum of 550 B.Th.U. per cubic foot in the case of the South Metropolitan Gas Co., down to 400 B.Th.U.; in the great majority of cases, however, the declared value is between 450 and 500 B.Th.U. Widely varying views are at present held as to the most economical calorific value for the supply, some regarding a much lower calorific power than 400 B.Th.U. as the most advantageous, and a much more extended experience of working under the new conditions will be necessary before a fairly general agreement can be come to between the conflicting views. There is little doubt, however, that the next few years will bring about considerable changes in methods of working from those contained in the present article, both in improvements of old, and development of new methods.

In the United States, and also in Canada, following on the development of the oil-fields and resulting cheap oil supply, the manufacture of coal gas was largely superseded by that of carburetted water gas, *i.e.* of a mixture of water gas and oil gas of approximately the same illuminating power and calorific power as coal gas, and in 1910 some 80 p.c. of the gas supplied consisted of carburetted water gas; since that date, however, the tendency has been in the direction of increasing the proportion of coal gas supplied. In this country also, from 1890 onwards, many gas undertakings have also manufactured carburetted water gas, which was mixed with the coal gas to an extent not, as a rule, exceeding 40 p.c. of the output of any individual undertaking.

In the year 1913, nearly 24,000 million cubic feet of blue-water gas, and carburetted water gas were made in the United Kingdom or 10·8 p.c. of the total production, and only a very small proportion of this was blue-water gas. Since that date the increasing scarcity and rising price of oil has brought about a large reduction of the amount of oil used in this way, and the addition of blue-water gas without oil enrichment has greatly increased, this being made either in separate plants or by the introduction of steam into the retorts during carbonisation. In 1919, the total amount of blue-water gas and carburetted water gas produced in separate plants amounted to 38,500 million cubic feet, or 15·8 p.c. of the total production; no figures are available as to the amount of water gas produced by steaming in the retorts, as this cannot be measured separately from the coal gas simultaneously produced, and is consequently included in the coal-gas figures. The amount of oil used, on the other hand, decreased from 58 million gallons in 1913 to 34 million gallons in 1919.

Gas coal. In this country, by far the largest proportion of coal employed for gas-making purposes is of the character known as bituminous caking coal, *i.e.* a coal which, in addition to yielding a large volume of gas, also forms a plastic mass during the early stages of heating, and then subsequently undergoes carbonisation, and results in the production of a coherent coke of good commercial value. The non-caking bituminous coals, even when yielding a large volume of gas, only give a poor coke, having the same shape and size as the pieces of coal carbonised, and having a low selling value. These are therefore only employed in cases where local conditions are such that non-caking coals are obtainable at a cost sufficiently below that of caking coals, to compensate for the lessened value of the coke produced. This is especially the case in Scotland, where the Scotch splint coals are often of a non-caking or only feebly caking quality.

A further exception to this rule also occurs in the case of cannel coal, which was formerly used in considerable quantity, as, although the coke obtained was almost useless, it gave a very large yield of gas of high illuminating power, and a certain proportion of cannel was therefore used in many works to enrich the gas given by poorer coals to the statutory quality. At the present time, however, very little cannel is employed: firstly, because the increasing scarcity of good cannel caused a rapid increase in its price some 30 years ago, on which account oil from petroleum was largely used in its stead for enrichment, either by making this into oil gas or carburetted water gas and adding these gases to the coal gas. In place of the use of cannel, the low-quality gas was also frequently enriched by carburetting with volatile hydrocarbon vapours, such as the low-boiling paraffins and benzene. In the second place, owing to the lessened importance of illuminating power, enrichment of the gas was largely given up, and the quality reduced to such a figure as can be obtained direct from the caking coals most readily procurable in the locality of the particular gas undertaking.

The rich cannel coals were chiefly obtained from the Wigan coal-field in Lancashire and the Lanark coal-field in Scotland, but the supplies are now largely exhausted. Poorer cannels are found to some extent in most of the other coal districts, but these often give little or no better yield and quality of gas than the bituminous coals, and also give rise to a very low quality of coke, and are therefore only used when the price at which they can be purchased is very low.

It is held by many that, in view of the fact that cannel coals are capable of giving much higher yields of crude oil when suitably carbonised than can be obtained from coal, cannel coals should be reserved for such crude oil production, and a good deal of experimental work has been carried out in this direction. Up to the present the process of such crude oil production from cannel and similar materials has not been carried out on a sufficiently extended scale to determine fully its commercial practicability.

Chief sources of gas coals. Gas coal occurs in all the coal-yielding areas, but the chief supplies occur in the Newcastle or Durham district, South Yorkshire, Lancashire, Derbyshire, and North Staffordshire. Smaller amounts are obtained from North Wales, South Wales, and Somerset. Generally speaking, in order to reduce the cost of carriage, a gas undertaking obtains its coal from the nearest field producing a suitable quality. In the London district, however, and also for the most part in the south and south-west of England, the main supply is drawn from the Durham field, the greater distance away of those collieries being more than counterbalanced by the fact that the coal is brought for the greater part of the way by coasting steamers instead of by rail, which reduces the rate of carriage.

The coals obtained from the different seams in the same district, and often even from the same seam, vary considerably in their properties from a gas maker's point of view, and with one and the same sample of coal, the gas results also depend greatly upon the conditions under which it is carbonised. Nevertheless, the coals from each district have, as a rule, certain characteristics which distinguish them from those of other localities. This is especially the case with the coals from the Durham field, these, for the most part, undergoing carbonisation more slowly than the others under similar conditions, and yielding a harder and denser coke. They also yield a thicker tar of higher sp.gr., and in general give a somewhat lower yield of ammonia. The North Staffordshire coals also yield coke of good quality, the gas coke from both these districts being, on the average, superior to that from Yorkshire, Derbyshire, and Lancashire coal.

Valuation of gas coal. The simple elementary analysis of coal, giving the percentages of moisture, carbon, hydrogen, oxygen, nitrogen, sulphur, and ash, affords but very little information as to its value for gas-making purposes. If, however, as first pointed out by Bunte (J. Gasbel. 1888, 31, 895), the figures for moisture and ash be eliminated, and the percentage composition of the actual coal substance calculated, it is possible to judge the general properties of the coal from the figures obtained.

St. Claire Deville published a table (below), giving the results obtained from five typical samples of coal, which were subjected to analysis and gas-making tests in the coal-testing plant of the Paris Gas Works. Coals of Type III (7·5–9·0 p.c. of O in the coal substance) represent the best type of gas-making coals, giving a good yield and quality of gas and also good coke. Coals of Types I and II produce much coke and a poor yield of gas, whilst with Types IV and V the gas results are

		Type I.	Type II.	Type III.	Type IV.	Type V.
100 parts of coal substance contain	Oxygen	5·56	6·66	7·71	10·10	11·70
	Hydrogen	5·06	5·37	5·40	5·53	5·64
	Carbon	88·38	86·97	85·89	83·37	81·66
	Nitrogen (approx.)	1·00	1·00	1·00	1·00	1·00
Moisture content of air-dried raw coal		2·17	2·70	3·31	4·35	6·17
Total weight of distillation products (p.c.)		26·82	31·59	33·80	37·34	39·27
„ „ coke		73·18	68·41	66·20	62·66	60·73
Gas, per cent. coal substance		13·70	15·08	15·81	16·95	17·00
Tar		3·40	4·65	5·08	5·48	5·59
Gas liquor		4·58	5·22	6·80	8·62	9·86
COMPOSITION OF THE GAS IN PER CENT. BY VOLUME.						
Carbon dioxide		1·47	1·58	1·72	2·70	3·13
Carbon monoxide		6·68	7·19	8·21	9·85	11·93
Hydrogen		54·21	52·79	50·10	45·45	45·26
Methane and nitrogen		34·37	34·43	35·03	36·42	37·14
Heavy hydrocarbons		3·27	4·01	4·94	5·58	5·54
Specific gravity of the gas		0·352	0·376	0·399	0·441	0·482
Gas consumption for equal candle power		132·1	111·7	103·8	102·1	101·8

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It is held by many that, in view of the fact

Fig. 1 gives a diagrammatic representation in plan of the main features of a gasworks capable of making from 10 to 15 million cubic feet of gas per day, and having connection both with rail and water, the works being divided into two completely separate sections, so far as manufacturing plant is concerned; the gas from each section, however, joins together at the inlet to the gas holders, which can be filled from either section. It very rarely happens, however, that the disposition of the site renders so symmetrical an arrangement possible.

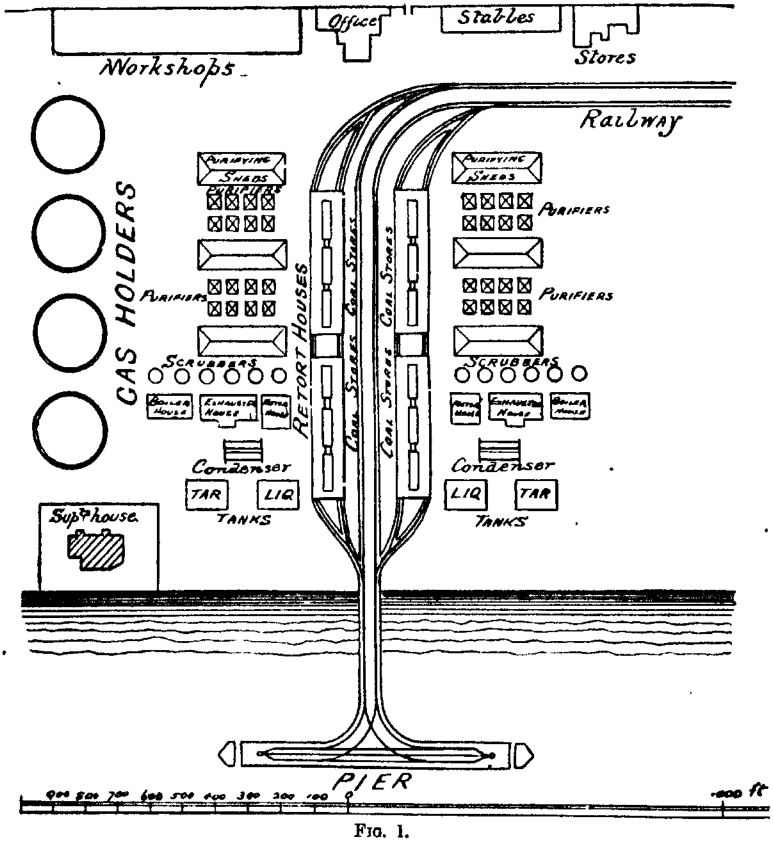

FIG. 1.

CARBONISATION OF THE COAL.

Broadly speaking, the process of carbonisation, which is by far the most important part of the manufacture, consists in subjecting the coal to distillation in closed vessels from which air is excluded, whereby it is split up into two portions, namely, a volatile portion which escapes from the retort, and by subsequent treatment yields tar, ammoniacal liquor, and permanent gas, and a non-volatile portion consisting mainly of carbon and the ash of the original coal, which remains behind in the retort as a porous mass of coke. The nature and amount of the constituents of the volatile products, as well as the composition and physical properties of the residual coke, depend not only on the nature of the original coal, but also to a large extent on the temperature employed for its carbonisation and on the manner in which the heating is carried out. The nature of the physical and chemical changes which occur is exceedingly complex, and these, so far as they have at present been elucidated, will be more conveniently considered after a description of the actual process of carbonisation as it is at present carried out in the majority of gasworks.

Manufacture of gas in horizontal retorts. The material employed for the manufacture of retorts consists at the present time almost universally of fireclay, and for modern carbonising conditions, the quality of the latter should be such that it will withstand temperatures up to 1300°–1400°, and should not develop serious cracks when subjected to such rapid alternations of temperature as inevitably occur when the hot retort is recharged with a cold mass of coal. The shape of the retorts is long and narrow, the length being from 9 to 10 feet when the retort is closed at one end, or from 18 to 22 feet when a 'through' retort is employed, closed by a mouthpiece and lid at each end, this last being now the plan mostly adopted in works of medium and large size. The width of the retort varies usually from 18 to 25 inches and the depth from 13 to 16 inches, the size 16-inch by 22-inch being probably used more than any other. The shape of cross section employed varies very considerably; in a few instances, circular retorts are employed (to which, of course, the above-mentioned dimensions of width and depth do not apply), in others oval retorts, but the majority have now a flat bottom and circular top and have approximately the shape of a half-inverted D, ⌓, and are commonly known as D-retorts, the corners between the bottom and sides being, however, always rounded, to facilitate the removal of the coke, and to render the retort less liable to crack. The thickness of the retort wall is 3 inches, increased to 4 inches at the end to facilitate the fixing of the iron mouthpiece and lid.

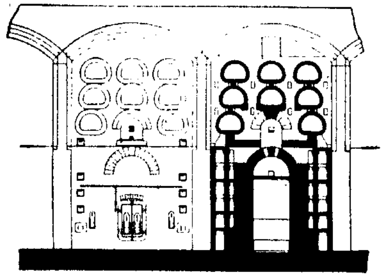

Fig. 2.

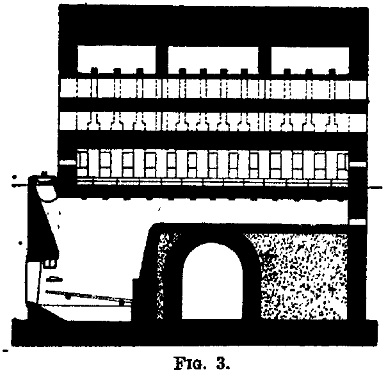

Fig. 3.

A number of these retorts are fixed horizontally in a single brickwork arch, the number in such a setting varying generally from 6 to 12. The retorts are supported by transverse brick walls, placed at intervals throughout the length of the retort, and extending to the top of the arch enclosing the setting, the method of construction being clearly shown in Figs. 2, 3, 4, and 5, which give diagrams showing the cross section and three longitudinal sections of a bed of eight through retorts. The gases by which the retorts are heated circulate around the retorts in each of the vertical chambers formed by the cross walls, travelling first upwards along the inner sides of the retorts, and thence over the top of the highest retorts and down along the outer sides of the retorts and away to the chimney.

The method formerly adopted for heating was that of direct firing, a shallow coke fire being maintained on a hearth placed in the centre of the setting below the middle retorts. With such firing the heating of the retorts is effected solely by the sensible heat of the products formed by the combustion of the carbon of the coke by the oxygen of the air, *i.e.* carbon dioxide, nitrogen, excess of oxygen, and in order to get the retorts properly heated in the part with which the gas last comes in contact, it is necessary that the temperature of the latter must not be below about 1000° when they pass away from the setting. As in addition, a considerable excess of air must be used to get complete combustion of the coke, this excess ot air likewise passes away to the chimney at a high temperature, resulting in great waste of fuel, and the actual consumption of coke for heating such direct-fired settings amount to 25–30 p.c. weight of coal carbonised.

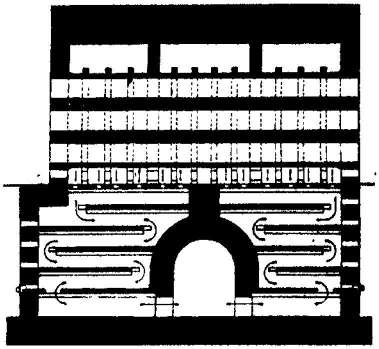

Fig. 4.

At the present time, in installations of any size, this method of direct firing has been abandoned in favour of gaseous heating. For this purpose, a deep producer is provided for each bed of retorts, as shown in Figs. 2 to 5, which is charged with hot coke, when required, by allowing the incandescent coke from the retorts to fall directly into it. A limited supply of air (primary air) is admitted below the furnace bars, and passing through the deep layer of coke, the oxygen is converted chiefly into carbonic oxide and to a smaller extent into the dioxide. Steam is introduced along with the primary air, as water is allowed to drip on to the furnace bars to prevent their burning through, and water also evaporates from that kept in the ashpan below the surface, and this steam is largely converted into hydrogen and carbon monoxide in passing through the incandescent fuel. The presence of steam lowers the temperature of the fuel in the generator, thus reducing wear and tear of the lining, and also prevents the fusion of the clinker formed from the ash, and renders it more readily removable. The composition of the gas varies according to the proportion of air and steam used, but generally approximates to the following example:—

Carbon dioxide . . .	5·2 p.c.
Carbon monoxide . .	24·4 ,,
Hydrogen	8·6 ,,
Methane	0·8 ,,
Nitrogen	61·0 ,,

The producer gas thus obtained consists to the extent of about two-thirds of incombustible gases, and is not an ideal one for obtaining very high temperatures; but it is, nevertheless, fully capable of developing the highest temperature required for carbonisation—this being made more easy by reason of the fact that it enters the setting already heated to a very high temperature. Further, as will be seen directly, the air required for its combustion also enters the setting at a moderately high temperature.

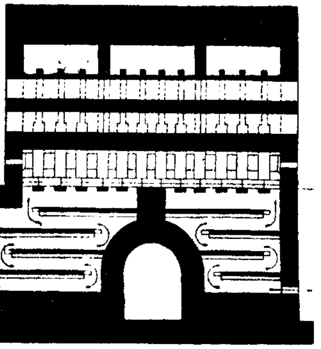

FIG. 5.

In very brief outline, the method of working the setting is as follows: The hot furnace gas collects above the coke, and then passes through nostril holes cut in the furnace arch; one or more nostril holes being placed at the bottom of each of the vertical spaces formed by the cross walls supporting the retorts (*see* Figs. 2 to 5). As it enters the setting, the furnace gas is met by the stream of secondary air necessary for its complete combustion; this being introduced by suitable flues so arranged that a supply of air meets each stream of furnace gas issuing from the nostrils in the furnace arch. Complete combustion of the gas takes place as the streams of furnace gas and air intermix in their circulation around the retorts; the heat thus evolved causing the temperature of the latter to be raised to the required point.

The waste gases leaving the setting have inevitably a high temperature, as they must be sufficiently hot to raise the temperature of the last portions of the retort with which they come in contact to the carbonising temperature required, and if allowed to pass direct to the chimney much loss of heat would ensue. To effect a partial recovery of this heat, the waste gases, on their way to the chimney, pass through the regenerator, which consists essentially of a series of flues adjacent to and separated by a thin fire-brick partition from a parallel set of flues through which the secondary air is allowed to flow on its way to the setting, travelling in the reverse direction to the waste-gas stream. Much of the heat of the latter is thereby transferred to the secondary air, and thus carried back into the setting, resulting both in economy of fuel and enabling a higher temperature to be obtained with a lower fuel consumption than would otherwise be the case.

The amount of primary air admitted to the furnace and of secondary air to the setting is controlled by suitable slides on the ports of admission and by dampers placed at the outlet of the regenerators. In a setting of through retorts, these last are usually four in number, each taking the waste gas from one quarter of the setting, so that by their adjustment, not only is the total amount of gases drawn through the setting controlled, but also the proportionate amounts drawn into the different parts. By suitable regulation of the primary air slides and dampers, the furnace is made to produce the requisite quantity of gas for the proper heating of the setting, and the secondary air slides are adjusted to supply as nearly as practicable the exact quantity of air required for the complete combustion of the furnace gas. With this method of heating the fuel, consumption is reduced to about one-half that required with direct firing, viz. from 12 to 15 p.c. of the weight of the coal carbonised, whilst simultaneously much higher retort temperatures are attainable.

The charging of the coal into the retort and the withdrawal of the coke produced were formerly always effected by manual labour, the coal being charged with the shovel, or by a scoop run into the retort by hand, and then inverted and withdrawn, the coke being drawn by a rake. This plan is still adopted in small works, where the magnitude of the operations is not sufficient to make the installation of machinery remunerative. In larger works, however, the operations are now usually effected mechanically, a considerable number of machines of different type being at present in use. Limitations of space, however, prevent anything more than a very general description of these machines. In the earlier machines, which were widely adopted, namely, the West and the Arrol-Foulis machines, the existing manual method was closely imitated by mechanical means, the charging machine for the coal inserting the latter by means of a scoop or similar contrivance, and the discharger removing the coke by a mechanically actuated rake; in the West apparatus, compressed air is used as the motive power; and in the Arrol-Foulis, hydraulic pressure. In more recent types of machine different methods are employed. Thus in the De Brouwer apparatus, a stream of coal is projected into the retort at such a high velocity that it is carried to a stop placed at the far end, and then built up in an even layer to the front of the retort; in place of raking out the coke, the plan now being adopted is that of mechanically pushing out the coke from one end, this method being, of course, only applicable to through retorts, which can be opened at each end. Other machines, such as the Fiddes-Aldridge, are also in use, which effect in one movement the discharge of the coke and the introduction of a fresh charge of coal, and at the present time electrical power is largely employed for actuating retort-house machinery.

In addition to the actual machinery employed for charging the coal and drawing the coke, additional mechanical equipment is also required in the retort house. The coal to be carbonised must not contain lumps of too large a size where machine charging is used, and is therefore dropped into a coal breaker, from which it falls into an elevator, and is raised to a height well above the retort benches, falling from the latter either direct or by means of a conveyor into storage bunkers, from which it is drawn by the charging machines as required. Mechanical conveyors of various types are also frequently employed for removing the coke from the retort house as it is discharged from the retorts, and to carry it to suitable screening machinery for sorting into different grades.

Inclined retorts. In order to utilise the action of gravity in charging and discharging retorts, the horizontal position of the retorts has been abandoned in many installations during the past 25 years, the retorts being set instead at an angle of about 32° to the horizontal, this being approximately the angle of rest of broken coal. Fig. 6 shows a longitudinal section of such a setting of inclined retorts. To charge them, a stop is placed at the lower end of the retort, and a stream of coal admitted at the top, which falls down the retort until it reaches the stop at the bottom, after which, with a properly regulated supply of coal, it builds up in an even layer to the top of the retort. To discharge the retort after carbonisation is complete, the stop is withdrawn from the bottom, when the coke should fall out by the action of gravity. Usually, however, a certain amount of assistance is required to start the movement, such as pricking with a bar, this being especially the case with retorts which have been at work for some time and have altered in shape.

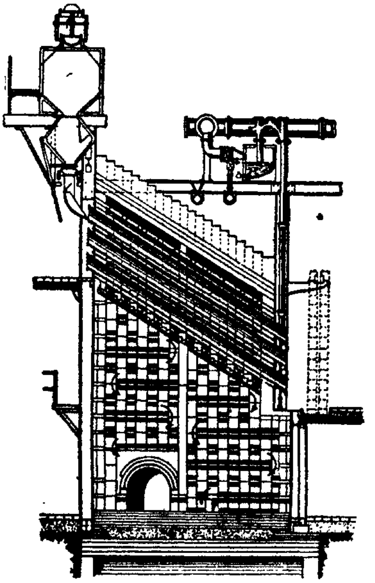

Fig. 6.

Inclined retorts were first adopted with practical success by Coze at the Rheims Gas Works in 1885, and have since been installed to a very considerable extent in most countries where the gas industry is established, including Great Britain. Here, however, it has never appeared probable at any time that the inclined retorts would altogether supplant the horizontal retorts, and during recent years but few new installations have been built, the improved machinery for charging and discharging the horizontal retorts having increased the favour with which these are regarded.

The relative advantages of the two systems refer almost exclusively to questions of capital cost, upkeep, and labour charges, and do not materially affect the matter of the yield and quality of gas, as the actual carbonisation of the coal, with proper working, takes place in the same manner in each case, the coal in both being heated in an even layer in the retort, with a considerable amount of free space above the coal, and the sequence of changes which take place from the action of heat is substantially the same in both cases.

Retort-house working. The weight of coal introduced into the retort varies naturally according to the size of the latter, but up to about the year 1900 the weight of charge placed into the retort of the most common size, namely, 20 feet long, 16 inches deep, and 22 inches wide, was between 6 and 7 cwts. (and a proportionate charge in retorts of other sizes); and with such a charge, even with coals which swell considerably during carbonisation, a sufficient amount of free space remained above the mass at the end to permit of the introduction of the rake-head to discharge the coke. The temperature within the retort varies in different works from about 900° to 1250°, the tendency being constantly in the direction of the higher figure, and the time required for the carbonisation of such a charge averages about 6 hours in the case of most caking bituminous coals, but is only about 4 hours with Scotch splint coals. The gas evolved during the first half-hour is somewhat low in quality, but in the succeeding $1\frac{1}{2}$–2 hours the yield of gas is highest both in quality and quantity. For the remainder of the time, the volume and quality steadily diminish, and when carbonisation is nearly complete, the small volume of gas evolved consists largely of hydrogen, with from 10 to 20 p.c. of methane and some carbonic oxide. In order, therefore, to obtain a stream of gas which is approximately uniform both in quantity and quality, and also to facilitate retort-house working, the retorts are not all charged together, but a certain proportion only are charged at regular intervals of an hour or two hours, according to circumstances, so that the carbonisation in the different retorts is at different stages at any particular time, and the mixture of gas formed by the combined streams from the retorts keeps more nearly uniform.

Treatment of the hot gases issuing from the retorts. In order to collect the evolved gases, a cast-iron mouthpiece is bolted to the mouth of the retort (or to both mouths of a through retort) having a hinged lid in front, which can be opened for the purpose of discharging the coke and putting in a fresh charge of coal, and then closed so as to form a gas-tight joint. An illustration of a 'self-sealing' mouthpiece in common use is shown in Fig. 7. On the top of the mouthpiece is cast a socket, into which is fixed a vertical pipe of from 4 to 8 inches diameter, termed the *ascension pipe*, extending upwards above the brickwork of the setting (Fig. 8). By means of the *bridge pipe*, this is connected with the *dip pipe*, which conveys the gas into the collecting main. A separate collecting main is usually now provided for each bed of retorts, the combined gas from each of these passing away by a pipe at the top or side into the *foul main*, by which the gas is conveyed from the retort house to the condensing and purifying plant. Two types of collecting main are in use, namely, the *hydraulic main* and the *dry main*.

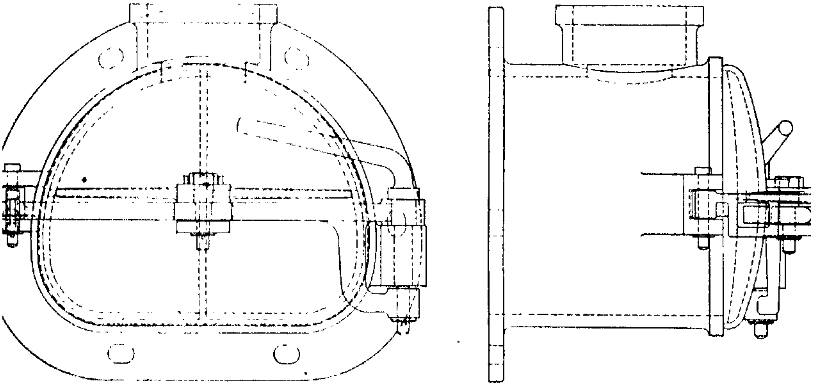

Fig. 7.

In the hydraulic main, which is most commonly employed, the tar and liquor condensed from the gas at this point are allowed to accumulate to such an extent that the dip pipes are sealed in the liquid, this seal then forming an automatic valve, which allows the gas made in the retort to bubble through it into the collecting main, but prevents any gas getting back from that main along the bridge pipe and ascension pipe, when the retort lid is open for purposes of charging. With the dry main the dip pipes are not sealed in the liquid, and in order to prevent gas passing back when the lids are open or air being drawn into the main through the open lid, some method of closing the pipe must be provided which can be operated when the lid is open. Several forms of valve are in use, but are apt to give trouble from the separation of thick tar and carbon on them, and, therefore, in other cases, arrangements are made whereby the dip pipe can be sealed in the liquid whilst the lid is open, and unsealed as soon as this is closed.

Where the hydraulic main is employed, matters are now so arranged in most works that the tar and ammoniacal liquor which separate in that main, are drawn off separately, the tar being taken away from the bottom as it separates, whilst the liquor flows away from an overflow, the height of which can be regulated as desired, the object especially aimed at being to ensure that the dip pipes are sealed in liquor, and not in tar or varying mixtures of tar and liquor. This separate removal of the tar and liquor may be effected in many different ways, a type of apparatus in common use being the Dillamore tar tower, shown in Fig. 9 (p. 318). This is placed at the end of a bench of retorts as shown, and serves a number of beds. The tar pipe runs from the bottom of each hydraulic main to about the middle of the tower, whilst the lighter ammoniacal liquor flows from a side opening near the upper level of the liquid in the hydraulic main to the top of the tower. The latter is also connected by an equilibrium pipe to the top of the hydraulic main, or foul main, the gas pressure in each being thus maintained the same, under which circumstances the upper level of the liquid is the same in both. The condensed liquor flows from the top of the tower over a weir valve, the height of which can be regulated to give any required depth of seal in the hydraulic main. The tar accumulates in the bottom of the tower, displacing an equal volume of liquor, which flows away over the weir valve, and is run off periodically, care being taken that its upper level never rises above the level at which the tar enters the tower. Whilst running the tar off, liquor must be run in from a tank to the top of the tower at a greater rate than that at which the tar is run off, as otherwise the level of the liquid in the hydraulic main would fall, unsealing the dip pipes.

In order to obtain good results in carbonisation, so far as yield and quality of gas are concerned, it is most essential that the gas pressure in the retort should be maintained as uniform as possible, and only slightly above that of the atmosphere, attention to this point being second only in importance to that of keeping good and even temperatures of the retorts. The necessity for this arises from the fact that the fire-clay retorts are themselves porous, and also develop cracks through the alternate heating and cooling, and hence, if the pressure within the retort exceeds that of the gases circulating round it to heat it, gas tends to escape through the pores and cracks, and is burnt around the setting and thus lost; and if, on the other hand, the pressure within the retort is materially lower than that within the setting, waste gases, consisting chiefly of nitrogen and carbon dioxide, are drawn into the retort and pass away with the gas made, and lower its quality. In passing over the hot retort walls, the gas, however, always undergoes a certain amount of decomposition, resulting in the deposition of carbon on the walls, which tends to block the pores and small cracks, and thereby to render the retort more gas-tight, the leakage being much higher with a new retort, or immediately after the removal of the crust of 'gas carbon' or 'scurf.' The latter process must be carried out periodically, as it otherwise becomes so thick as to interfere with the proper heating, as well as with the charging and discharging of the retort, the gas carbon obtained finding a ready sale for the manufacture of electrodes.

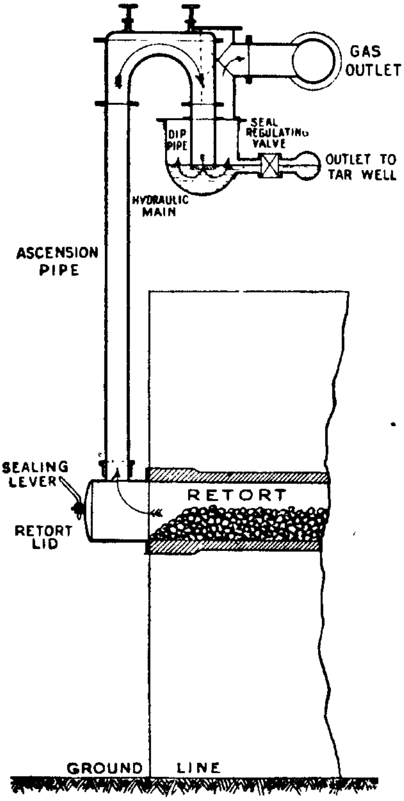

Fig. 8.

A very considerable pressure is required to pass the gas through the condensers, scrubbers, and purifiers, and into the holders, and if the whole of the necessary pressure were thrown on the retort, most of the gas would, in large works, be lost into the setting, and, therefore, in all but very small works a pump or exhauster is employed to draw the gas from the retorts as it is made, and to force it on through the subsequent apparatus and into the holders. The exhauster is run in such a manner as to maintain the gas pressure constant in the hydraulic main above the liquor level, and in addition an automatic retort-house governor is also frequently employed to ensure that this pressure is maintained as uniform as possible. Even then, in order to ensure that the pressure in the retort itself is maintained constant, great care must be exercised in maintaining the hydraulic main exactly level, and the dip pipes of equal length, as otherwise the depth to which these are sealed in liquor will vary, and, consequently, the pressure in the retorts, which is equal to that in the hydraulic main less the depth of the seal, will also vary, so that some may be losing gas to the setting and others drawing furnace gas into the coal gas. Where the latter is the case, the pressure in the retorts and ascension pipe is below that of the atmosphere, and, consequently, when the retort lid is opened, air is sucked into the gas through the ascension and dip pipe, thus further reducing its quality.

Even when the hydraulic mains are level and the dip pipes sealed to an equal extent throughout, and the pressure in the hydraulic main is maintained constant, the bubbling of the gas through the liquid causes a rapid oscillation of the pressure within the retort, which may be considerable. By careful attention and regulation of the depth of seal, this oscillation can be very greatly reduced, but never altogether eliminated, and in this respect the dry main, in which there is no seal for the gas to bubble through, has the advantage. On the other hand, the fact that the seal forms an *automatic* valve, which does not require to be operated by the workman when opening and closing the lids, and also that where a dry main is used, more trouble is often experienced in getting the thick tar to flow properly from the mains, especially with some types of coal, has led to the hydraulic main being most frequently adopted in spite of the above objection.

Chemical Changes occurring during Carbonisation.

The essential elementary constituents of coal are carbon, hydrogen, and oxygen, and, in addition, smaller amounts of nitrogen and sulphur are always present, as well as varying amounts of mineral matter, which remains behind as ash when the coal is completely burnt. With regard to the chemical constitution of the doubtless numerous compounds present in coal, little definite evidence is as yet available. There is general agreement that the substances have been formed slowly from the large deposits of vegetable matter of the carboniferous period, the changes taking place generally in absence of or with only limited access of air, and that both temperature and bacterial action have played a part in its production. It is also generally agreed that the larger proportion of the substances forming the existing coal have been derived from the "cellulosic" constituents of the original vegetable matter, and that the smaller proportion consists of substances derived from the waxes and resins of that material. F. Fischer and Schrader (Brennstoff-Chemie, 1921, 2, 37) have suggested that the true cellulose of the original matter plays no part in the substances remaining now in the coal, but has been completely resolved into gases and disappeared, and that the "cellulosic" constituents are derived solely from the lignin content of the original material.

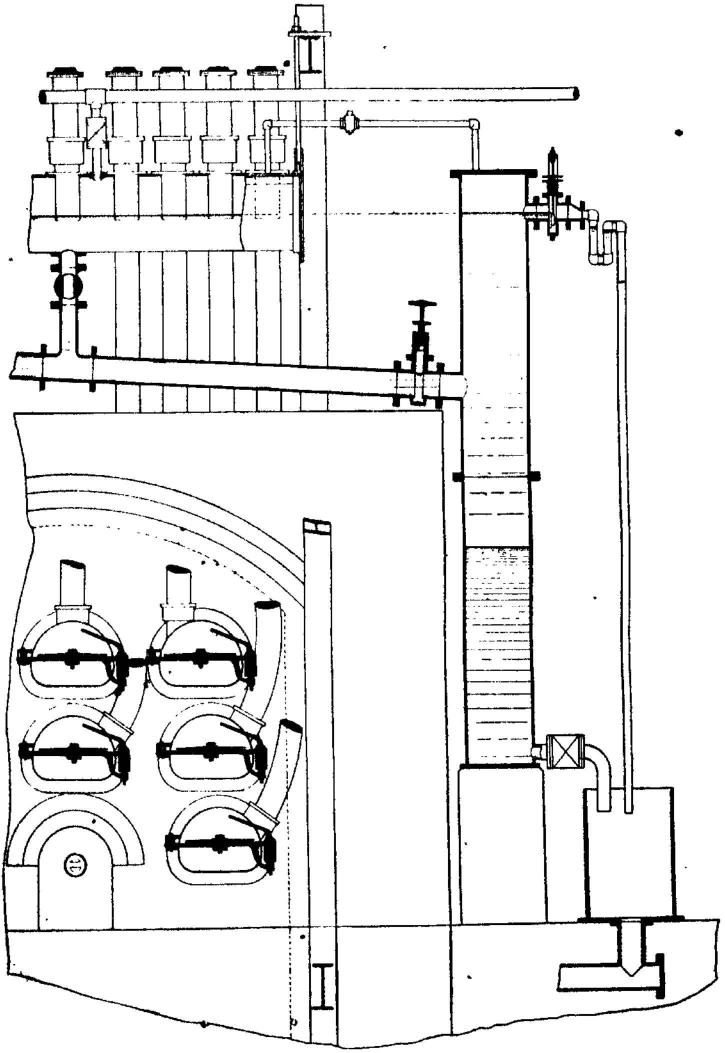

FIG. 9

In any case, the compounds as they now exist, whether formed from the woody or the resinous constituents of the original vegetable material, are of very high molecular weight. Neutral solvents such as alcohol, benzene, &c., extract only exceedingly small amounts of soluble matter from the coal. The basic solvent pyridine is, however, much more effective (Bedson, J. Soc. Chem. Ind. 1908, 27, 147; Burgess and Wheeler, Chem. Soc. Trans. 1911, 99, 649), have shown that with this solvent varying amounts up to 35 per cent. of soluble matter may be extracted. It is, however, doubtful if this extracted matter consists of substances actually present in the coal, as it is very probable that the chemically active liquid pyridine first effects some resolution of the substances present in the coal into those of lower molecular weight, some of which dissolve in the pyridine. Good gas-making coals generally give a high percentage of such pyridine soluble matter.

The changes which take place when coal is heated in absence of air are exceedingly complicated in character, and result in the production of an immense number of different substances, some gaseous, some liquid, and some solid at the ordinary temperature. The liquid constituents, which condense together in the form of coal tar, are by far the most numerous, the different compounds isolated from it already being numbered by hundreds, and doubtless large numbers of unknown compounds are also present (*v.* TAR). Moreover, both the nature of these substances and their relative amounts in the products vary greatly according to the temperature to which the coal is heated, and the manner in which the heat is applied, and our knowledge of the nature of the reactions occurring during the process is still very far indeed from complete, so that it is only possible as yet to discuss these changes in very broad outline.

When coal is heated, except for evolution of water, and small quantities of oxides of carbon, no apparent change takes place below 300°, but the available evidence points to the conclusion that some changes take place below the apparent point of decomposition which result in the dissociation of many of the substances present into others of lower molecular weight, as many coals and bituminous shales if heated for some time below their apparent decomposition point, yield a largely increased quantity of soluble matter on extraction with neutral solvents. At temperatures varying from 300° to 350° with different coals decomposition commences with evolution of volatile products, the larger proportion of which condenses to liquids at the ordinary temperature, and only a small proportion of which forms permanent gases. These last consist chiefly of carbon dioxide, carbon monoxide, and gaseous hydrocarbons, with little, if any, hydrogen.

By carrying out the decomposition at the lowest possible temperature in a high vacuum, Pictet, Ramsayer and Kaiser obtained a tar from which they were able to isolate a series of hydrocarbons all of which belonged to the cycloparaffin series, the lowest of which was hexahydrotoluene, C_7H_{14}, and the highest $C_{13}H_{26}$. They were also able to isolate the same hydrocarbons from the extract obtained by long continued extraction of large amounts of Montrambert coal with benzene. Hence it seems probable that these hydrocarbons are either present as such in coal, or in such a state of combination that they are readily dissociated from the combination. In addition the "vacuum-tar" contains considerable amounts of oxygen compounds; the major portion of these consist of the higher homologues of phenol, phenol itself being absent or present in only minute amount. Acids containing the carboxyl group are also present in small proportion, and a larger proportion of neutral oils containing oxygen whose constitution is unknown.

When the coal is carbonised, whether on the small or large scale, at temperatures not exceeding 400°–450°, the general character of the tar and gas produced is similar to that above described, although, of course, secondary decomposition of the primary products must occur to a somewhat larger extent, these conditions representing what is now generally termed "low-temperature carbonisation." The yield of tar with "gas-coals" varies from about 8 to 10 p.c., and the gas yield from 3000 to 4000 cubic feet per ton of high calorific power, consisting to the largest extent of methane, ethane, &c., and only moderate percentages of hydrogen. The saturated hydrocarbons in the tar are to a large extent of the cycloparaffin series, but some hydrocarbons of the paraffin series are also present. Unsaturated hydrocarbons are also present in quantity, chiefly olefines, but there is always also a fair proportion of those of the C_nH_{2n-2} series, especially of the dienes, as well as cyclopentadiene and its homologues, but unless the temperature exceeds about 600°C., aromatic hydrocarbons are almost entirely absent.

The physical character of the residue varies greatly according to the character of the coal. Where the coal contains constituents which are fusible, the melting of these converts the coal at temperatures rather above 300° into a plastic or semisolid mass, which then undergoes decomposition leaving a porous coherent coke. Where the constituents do not fuse before decomposing, the residue remains of the same shape as the original coal. In both cases the residue still contains considerable percentages of volatile matter, and burns in the air with a flame but without production of smoke.

Where the chief object is to obtain smokeless fuel from coal or carbonaceous products, or where the special aim is the maximum production of oil from the material, such low-temperature carbonisation may be advantageous. The yield of gas under these conditions is, however, so low (although of high calorific power) that the employment of such low temperatures is not as a general rule commercially practicable, and for this purpose higher temperatures must be employed when the gas is the chief product required.

In considering the changes which take place at such higher temperatures it is most convenient to deal first only with the carbon and hydrogen of the coal which are the most important constituents from a gas-making point of view. When the closed vessel into which the coal is placed is heated to a higher temperature, it only rises in temperature slowly, and therefore at first only undergoes the above low-temperature decomposition. The further action of heat then brings about fresh changes, both in the above hydrogen-containing residue and in the volatile substances primarily evolved from the coal. The effect of further heat on the residue is to drive off more hydrogen, which, at temperatures of 700°-800°, is mostly evolved as methane and free hydrogen, the latter being present in larger proportion, the amount of other gaseous hydrocarbons being very much smaller than in the gas produced at low temperature. The residual coke becomes denser and harder, but at this temperature still contains hydrogen in appreciable quantity, and on raising the temperature to the highest obtainable in practice, an additional yield of gas is procured still consisting of methane and hydrogen, but as the temperature increases the percentage of methane falls and that of hydrogen rises. The higher the temperature to which the residual coke is finally heated, the greater is therefore the yield of combustible gas.

The volatile products first evolved from the coal, consisting chiefly of compounds which are liquid at the ordinary temperature, also undergo further change when a higher carbonising temperature is employed, if they are subjected to the action of this heat before they can escape, the hydrocarbons contained in them yield a large proportion of gases which are permanent at the ordinary temperature, the most important of these being hydrogen, methane, and ethylene. At temperatures above 650°, aromatic hydrocarbons are produced, and if the temperature does not much exceed 700°, only those containing one benzene nucleus, *i.e.* derivatives of benzene itself, appear to be formed in material amount, such hydrocarbons as naphthalene and anthracene being almost entirely absent in the tar formed at these temperatures. The exact manner in which the production of these benzene derivatives occurs is as yet in doubt. It has been suggested that they are formed by loss of hydrogen from the naphthenes present, containing a ready-formed ring of six carbon atoms, or that they are formed by reduction from the phenolic bodies which are simultaneously produced from the oxygenated constituents of the coal. Whilst it is likely that some of the benzene derivatives are produced in these two ways, the fact that at the above temperatures approximately the same extent of production of benzene derivatives occurs with any carbonaceous matter, even from open-chain hydrocarbons, and in absence of any oxygen compounds or of naphthenes, makes it improbable that anything like all of these derivatives are obtained in this manner. Thus when American petroleum containing but little cycloparaffins and phenol, is cracked for the manufacture of carburetted water gas at temperatures of 750°, the proportion of aromatic hydrocarbons found in the tar produced is quite as high as that obtained when oils largely consisting of cycloparaffins are used. The most probable supposition on the evidence at present available, is that at the temperatures which result in the production of the benzene derivatives, the various hydrocarbons undergo decomposition to the extent of producing the single-atom unsaturated hydrocarbons $\cdot CH_3$, $:CH_2$, $\vdots CH$, capable of temporary existence, as shown by Sir J. J. Thomson in his positive-ray analysis of methane, and of analogous molecules such as $\vdots C\cdot CH_3$, and that the benzene derivatives are produced by the subsequent union especially of these molecules to form the benzene ring, which when once formed is known to be exceedingly stable towards heat. At such temperatures benzene itself forms only a moderate proportion of the aromatic derivatives produced, the homologues with one or more side chains being produced in larger quantity.

As the temperature to which the volatile products are subjected is further raised, there is an increasing tendency to the production of benzene itself by the elimination of the side chains from the toluene, xylene, &c., and simultaneously complex aromatic hydrocarbons containing more than one benzene nucleus make their appearance, and the higher the temperature the larger are both the quantity and the complexity of the products, many of which are now of very high molecular weight, and for the most part infusible and insoluble, and therefore remain suspended in the tar produced, forming what is commonly termed the 'free-carbon' in the tar. Saturated aliphatic hydrocarbons largely disappear, and the quantity of dienes falls, but olefines still remain present in considerable quantity.

At these latter temperatures, the effects on the gas production are by no means altogether favourable, as although some hydrogen is produced in the changes which the volatile products undergo, the simpler gaseous hydrocarbons which form the most important constituents of the gas themselves undergo decomposition into hydrogen and carbon, which last is deposited partly on the coke and partly on the walls of the retorts as 'carbon' or 'scurf,' and this material, although of some value, is of greater worth if left in the gas in the form of hydrocarbons. The presence of the solid 'free-carbon' in the resulting tar also greatly increases the difficulty of retort-house working by forming deposits in the mains, &c., which are only removable with difficulty.

The chemical considerations therefore lead to the conclusion that while in order to obtain from coal the maximum yield of energy in the form of combustible gas, it is advisable to subject the latter finally to as high a temperature as possible, so as to drive off the volatile matter completely, the gases and vapours produced in the distillation should only be subjected to a considerably lower temperature than that to which the coke is eventually heated, as too high a temperature results in the separation of carbon, which would otherwise have remained as gaseous hydrocarbons in the gas; thus depreciating both its calorific and illuminating power. On the other hand, it is equally evident that these volatile products must not be subjected to too low a temperature, for in that case the hydrocarbons, &c., produced in the early stages of distillation would not be sufficiently decomposed, and would be lost from a gas-making standpoint—being condensed in the tar.

The remaining constituents of the coal concerned in the production of gas are oxygen, nitrogen, and sulphur. The ash remains in the coke, and need not be further considered here. Oxygen is present in considerable amount in the coal substance; and the coal as used also always contains either moisture in the free state or in such a loose state of combination that it is given off at temperatures below 100°—the amount varying usually from 1 to 7 p.c. The low-temperature carbonisation first taking place results, as stated above, in the resolution of the oxygen-containing constituents of the coal into carbon dioxide, carbon monoxide, and steam, and condensable compounds of carbon, hydrogen and oxygen largely consisting of the higher phenols. The further action of heat on these last results partly in the elimination of the side-chains and production of lower homologues and of phenol itself, and in addition the action of these on the heated carbon results in some of them losing their oxygen and yielding the corresponding aromatic hydrocarbon. The resulting tar at high temperatures always still contains considerable percentages of phenols, the amount relative to the coal carbonised always increasing as the percentage of oxygen in the coal used increases. As the temperature rises, the carbon dioxide tends to combine more and more with the red-hot carbon present, undergoing reduction to carbon monoxide, and the steam tends also to act on the carbon, with production of water gas; and the higher the temperature to which the gases are heated, especially while in contact with the coke, the greater is the amount of carbon monoxide formed, and the higher also the amount of steam converted into water gas. In high temperature carbonisation, therefore, a small proportion of the oxygen in the original coal is recovered in the tar as phenol, etc., but the bulk of it remains as steam, which condenses out on cooling, and, roughly, about one-fourth is found in the gas as oxides of carbon.

The effect on the nitrogen is similar to that on the hydrogen. At very low temperatures some ammonia is given off, and also substances containing carbon, hydrogen, and nitrogen, which condense in the tar; while a large proportion of the nitrogen remains in the residue. At higher, but still moderate, temperatures, much more nitrogen is given off from the coal, and the above volatile products are largely broken up, with the formation of ammonia and some free nitrogen; and at such temperatures the maximum yield of ammonia is obtained. At still higher temperatures, more nitrogen is evolved from the coke; but the ammonia itself is then largely decomposed into its elements nitrogen and hydrogen, and also reacts with the hot carbon, producing hydrocyanic acid; and, in spite of the more complete elimination of the nitrogen from the coke, the yield of ammonia is decreased. In ordinary gas-works practice in horizontal retorts, only from 14 to 17 p.c. of the nitrogen in the coal is mostly recovered in the form of ammonia (*v.* AMMONIA). Some of the nitrogen is also found in the tar, chiefly in the form of nitrogenous bases, such as pyridine.

The sulphur, too, probably comes off first as compounds with carbon, and hydrogen; and these, when more strongly heated, yield sulphuretted hydrogen, which can be removed from the gas without much difficulty. At still higher temperatures, however, the decomposition of these volatile organic sulphur compounds takes place with formation of larger quantities of carbon disulphide; this compound being also produced, but probably in much smaller amount, in the gases last driven off from the coke, due to the sulphur still remaining in the latter. High temperatures, especially if allowed to act fully on the volatile products, therefore tend to increase considerably the amount of this impurity, which can only be removed with difficulty.

Both with regard to sulphur and nitrogen, therefore, as well as in the case of the hydrocarbons, it is desirable that the volatile products themselves shall only be heated to a moderate temperature if a maximum yield of the valuable product (ammonia) and a minimum yield of the deleterious impurity (carbon disulphide) is to be obtained. In the case of the oxygen compounds alone does there appear to be any advantage in subjecting these products to a high temperature, owing to the larger proportion of carbon monoxide and smaller proportion of carbon dioxide produced, as well as to the larger amount of steam converted into combustible gas. On the whole, the advantages gained in the latter respect are more than counterbalanced by the deleterious action of such high temperatures so far as the hydrocarbons and the nitrogen and sulphur compounds are concerned.

While, therefore, the effect of heat on coal, and generally on substances containing carbon and hydrogen, is primarily to resolve the compounds into simpler substances, the changes which take place finally are largely synthetical, and new substances are produced in large measure by the combination and interaction of the primary decomposition products, the nature and amount of the new substances formed varying greatly according to the conditions of carbonisation, and especially with the temperature to which they are heated and very greatly with the length of time during which they are exposed to that temperature. In addition to the synthetic production of new hydrocarbons already referred to, others occur in which different constituents are concerned. The formation of carbon monoxide by the action of the dioxide on carbon, and the synthesis of water gas by the interaction of steam and carbon, have been referred to. In addition, there is some evidence that methane may also be formed to a certain extent in the carbonising process by synthesis from hydrogen and carbon monoxide, in accordance with the reversible reaction $CO+3H_2 \rightleftharpoons CH_4+H_2O$. This reaction occurs almost quantitatively when a mixture of the gases is passed over metallic nickel at 250° (Sabatier and Senderens, Compt. rend. 134, 514), and although, as the temperature rises, the reverse reaction takes place in increasing degree, the evidence available points to the conclusion that appreciable amounts of methane are formed in this manner under some conditions during carbonisation.

In the carbonisation of coal in the most usual gas-works practice, the coal, as above described, is placed in a long narrow retort set either horizontally or at an angle of about 32° to the horizontal, leaving a considerable amount of free space above the coal through which the evolved gas must pass to reach the exit pipe at one or both ends of the retort. The carbonisation commences on the outside of the mass—namely, at the bottom and sides—where it is in contact with the heated retort wall, and also at the top, where it is affected by the heat radiated through the free space from the hot crown of the retort. The coal on the outside first becomes pasty and agglomerates, and then undergoes the low-temperature decomposition already described, the resultant vapours and rich gas escaping fairly readily into the free space above the coal. Here they are subjected to the further action of heat in two ways—namely, by contact with the heated walls of the retorts, and also by the action of the radiant heat rays which are traversing the free space. The net result of their combined action is to raise the temperature of the vapours passing through the free space, and to bring about much change; and the higher the temperature to which the retort walls are heated, the greater is the amount of further decomposition that they undergo.

The further action of heat on the pasty mass on the outside of the charge converts this eventually into coke; heat passing simultaneously further into the charge and converting the layer below into the pasty condition, which is assisted by the condensation on these lower layers of some of the tarry matters formed by the decomposition of the hotter layers above, and the extent to which such condensation occurs doubtless has much influence on the physical properties of the resulting coke. This sequence of changes continues until the heat has penetrated to the centre of the mass, and effected its complete carbonisation. After the first layer of hot coke has been formed, the gases produced from the interior of the charge, in order to escape from the retort, must not only undergo the ordeal of heat in passing through the free space, but also pass through the hot layer of coke on the outside of the charge; and the temperature and area of this coke mass constantly increases as time goes on. Further, as carbonisation proceeds, the rate at which the gas is evolved decreases, and in consequence, its speed through the free space becomes less, and it is exposed to heat there for a greater length of time. From all these causes, the quality of the gas falls off after the first hour, and especially when the carbonisation is approaching completion. The percentages of methane, ethylene, benzene, sulphuretted hydrogen, and carbon dioxide steadily diminish as time progresses, and that of hydrogen steadily increases; while that of carbon monoxide varies less considerably, as shown by the following table, giving the analysis of the gas evolved at different stages from a retort charged with Derbyshire coal, the temperature of carbonisation being about 950°:—

	Hours after commencement				
	½ hour	1½ hrs.	2½ hrs.	3½ hrs.	5 hrs.
Sulphuretted hydrogen .	3·8	3·1	2·8	2·1	1·2
Carbon dioxide .	3·0	2·8	2·6	2·3	1·7
Ethylene and benzene .	8·6	5·2	3·6	2·4	0·0
Oxygen . .	0·0	0·0	0·0	0·0	trace
Carbon monoxide	4·4	5·0	4·9	4·5	3·8
Methane . .	49·7	42·0	39·4	37·5	26·3
Hydrogen .	29·8	37·5	42·2	46·2	60·8
Nitrogen (by diff.)	0·7	4·4	4·5	5·0	6·2

Before the introduction of gaseous firing, the retort temperatures obtained in practice did not usually exceed about 900°C., or 1650°F. Under these conditions, the volatile products were not materially overheated, and gas of high illuminating power was produced; while the tar simultaneously formed was fairly fluid, and only contained moderate amounts of the objectionable 'free carbon.' The quantity of naphthalene formed was also not excessive, and that of 'light oils' simultaneously produced was, in most cases, sufficient to wash the naphthalene out of the gas during condensation to a sufficient extent to prevent its subsequent deposition in the solid state in the mains and services. On the other hand, under these conditions, a relatively low yield of gas per ton is obtained, as an appreciable quantity of volatile matter is left in the coke.

When, with the aid of gaseous firing, higher carbonisation temperatures were employed, matters were considerably modified, as the volatile matter of the coal was more completely evolved with the production of a greater volume of gas. But, as we have seen, it follows inevitably that, in a horizontal or inclined retort having a large free space above the coal, the volatile products must also be more strongly heated by an increase in the retort temperature; and, as a result, under these conditions, the gases and vapours undergo a more far-reaching decomposition than before, and a reduction in the quality of the gas is brought about. Some of the hydrocarbons formerly present in the gas are now deposited in solid or liquid form, which either remain in the retort as carbon or are condensed with the tar, and are lost from a gas-making point of view. Simultaneously, other disadvantageous changes occur, inasmuch as the tar produced is thicker and contains much more 'free carbon,' thereby increasing the trouble from stopped ascension pipes and pitched hydraulic mains, and greatly increasing the practical difficulties of retort-house working. Further, the action of these high temperatures on the volatile products increases the production of naphthalene and decreases that of light oils, and renders the cooled gas much more liable to deposit solid naphthalene in the mains and services both on the works and in the district, causing serious trouble both to supplier and consumer.

In spite of these last-named drawbacks, the employment of higher temperatures has, on the whole, proved favourable: the increased yield obtained from the more complete elimination of the volatile matter of the coal having more than counterbalanced these disadvantages. Nevertheless, a process of carbonisation is very desirable, in which the coal itself can be heated to a high temperature without simultaneously causing too great heating of the volatile products; and it is largely with a view to this end that modifications of the method of working have been introduced during the past few years.

From what has been said, it is clear that one of the chief causes of the overheating of the gases and vapours is the existence of a large free space above the coal in the retort. With the horizontal retort, so long as the coke had to be extracted by a rake, worked either by hand or mechanically, a considerable amount of free space was necessary in order to afford room for the introduction of the rake-head above the coke; but the invention of mechanically propelled pushers, which discharge the coke by pushing from one end of the retort, has done away with the necessity of the free space for the removal of the coke, and has made it possible to put in a much larger charge of coal without increasing the difficulties of discharging the latter. In recent years, therefore, by the introduction of such increased charges, the amount of free space has, in many works, been largely reduced in horizontal retorts, so that the gases and vapours are exposed to a smaller amount of retort surface, and, still more important, owing to the volume of the free space being smaller, they pass through it more quickly, and are exposed to the action of the heat for a shorter time. As the practical result, it is found that the coke produced is larger, a thinner tar containing less free carbon is produced, owing to the lessened overheating, less carbon disulphide is produced, less trouble from naphthalene ensues, and retort-house working is considerably facilitated. Whether the total heat value of the gas obtained from a ton of coal—*i.e.* the multiple of gas per ton × calorific power—is greater than can be obtained with the smaller charges, is a matter on which different opinions prevail at present.

On the other hand, owing to the increased thickness of the charge, a longer period must be allowed for its carbonisation if the central core is to be completely carbonised; and beyond a certain weight of charge, varying apparently with different classes of coal, the gas production per retort per 24 hours falls off, or can only be maintained by increasing the carbonisation temperature above that employed with the smaller charges. Such higher temperatures also increase the heat to which the gases are exposed in the free space; but experience seems to show that the effect of such increase is small when the volume of free space is low, or, in other words, that in bringing about decomposition of the volatile products the time during which the gas is exposed to heat is much more important than the temperature of the retort walls.

Carbonisation in vertical retorts. But, while the amount of free space can be in this manner greatly reduced, it is scarcely practicable to eliminate it altogether in horizontal retorts. If, however, the retort is placed in a vertical instead of a horizontal position, this is readily effected; as, in the nature of things, the coal when charged in from the top must completely fill the retort. Although a small amount of free space may be left at the top, matters can be so arranged that this is not too large and that the retort walls at this point are not heated to any great extent. Hence latterly carbonisation in vertical retorts has been much investigated, and is now practised in a steadily increasing number of works.

Intermittent vertical retorts. In the Dessau vertical retort system, patented by Bueb (Eng. Pat. 1393, 1904), the previous practice is adhered to, in so far that the coal is charged into the retort from an overhead hopper all at once, and allowed to remain there until carbonisation is complete, when the coke is discharged by gravity and the retort refilled with fresh coal. The retorts are either 4 or 5 metres in length, having an oblong cross section with rounded corners and are tapered, increasing in size from top to bottom to facilitate the discharge of the coke. Until recently 10 or 12 retorts were set in rows of two in a setting, each setting being heated by gas from a separate deep producer capable of being filled much above the point at which the producer gases are drawn off, so that it may run for 24 hours without recharging. Fig. 10 gives a vertical section of such a setting and producer, showing clearly the general arrangement of the plant.

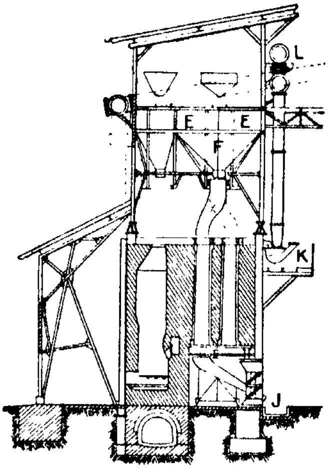

FIG. 10.

As the thickness of the charge is greatest at the bottom, the highest temperature is maintained at this point, with a rather lower temperature in the upper portions where the thickness of the charge is less. The result of this arrangement is that, even at high temperatures, not only is a large yield of gas obtained, but at the same time the tar formed is very fluid, and only contains a small percentage of free carbon. Simultaneously, the naphthalene production is lessened, and that of the lower boiling tar constituents increased, with the result that the naphthalene is sufficiently completely removed from the gas in the ordinary process of condensation, without the adoption of any special treatment, and, at the same time, the amount of sulphur obtained in the form of carbon disulphide is reduced. The yield of ammonia is also higher, and the coke produced is harder and denser than that formed from the same coal in horizontal retorts.

In spite, therefore, of very high retort temperatures, the objectionable overheating which occurs with horizontal retorts having a highly heated free space above the coal, is obviated in such vertical retorts. This is largely due to abolition of this free space, but other conditions also come into play. In the horizontal retorts, after a layer of incandescent coke has been formed on the exterior of the charge, all gas produced from the unaltered coal in the centre of the charge must find its way out through the incandescent layer, and thus be subjected to considerable heat. In the intermittent vertical retort, the carbonisation also takes place from the periphery inwards, and a layer of incandescent coke is formed in the early stages, but in this case the gas produced from the still uncarbonised coal in the centre of the charge has two possible paths of escape—on the one hand, through the hot coke layer, and on the other, through the cool central core of uncarbonised or partly carbonised coal, and the gas travelling in the latter direction escapes overheating by the hot coke layer. The relative amounts of the gas which travel in each direction is still a matter in dispute, but the evidence available leads to the conclusion that with coals which become pasty on heating, much the largest proportion of the gas travels through the hot coke, as the plastic coal film formed between the carbonised coke and uncarbonised coal in a more or less continuous layer is almost impermeable to gas, and as the greater gas production takes place on the coke side, where it is subjected to the greatest heat, the gases produced find their easiest route to the outlet at the top of the retort through the hot coke layer, which is always broken and fissured. On the other hand, where a non-caking coal is carbonised in vertical retorts, no such plastic layer forms, and with such coals unless the coal itself is very small and lies in a compact mass, the volatile products then mainly pass as formed to the outlet at the top of the retort through the cool core of uncarbonised coal.

In the later form of the Dessau retorts, the length of the oblong cross section has been reduced, and these retorts set in rows of three, which are charged and discharged simultaneously. The reduction in the size of the retort increases the proportion of heating surface to the cubic capacity of the retort, and results in a more rapid carbonisation and increased output of gas, and also a reduced fuel consumption.

Continuous vertical retorts. In this system of carbonisation, the object aimed at is not only to avoid an excessive heated free space above the coal, but also to render the process a continuous one, by the addition of mechanical arrangements whereby the coke is withdrawn continuously, or nearly so, from the bottom of the retort, fresh coal being added to the retort at the top to replace the coke withdrawn, so that the coal to be carbonised slowly travels down the retort, undergoing gradual conversion into coke and gas. The conditions in the retort, therefore, remain approximately constant, and the quantity and quality of the gas evolved remains fairly constant, instead of both falling off as carbonisation proceeds, as is the case with an intermittently charged retort.

The continuous system of carbonisation has been chiefly worked out in this country. Although many experiments in this direction were made in the last century, none met with any degree of success. In the early years of the present century, however, very interesting results were obtained with the Settle-Padfiled continuous vertical retort (Eng. Pat. 12552, 1902; 24588, 1903), which showed that excellent carbonising results, so far as yield and quality of gas and coke were concerned, could be obtained in this manner, although, largely owing to difficulties arising from the shape of retort adopted, the practical difficulties found in working it have prevented its further adoption. At the present time several such continuous processes are in use, the most widely adopted being the Woodall-Duckham system (Eng. Pat 16497, 1903; 15053, 1907) and the Glover-West system (Eng. Pat. 23650, 1905; 2663, 1907; 7534, 1907; 8572, 1909), a diagrammatic section of each of these plants being shown in Figs. 11 and 12, from which the general arrangement is readily seen. In the Woodall-Duckham retorts, Fig. 11, the discharge of the coke is controlled by the coke-feed roll shown below the retort, which is slowly revolving, and as it rotates allows the coke to fall into the chamber below, from which it is emptied periodically, the speed of the coal through the retort being regulated by varying that of the feed roll. As the coke is removed, the whole mass in the retort falls, leaving a space at the top, which is at once filled by fresh coal introduced from a small hopper above each retort, connected by a valve with the main coal bunker above from which it can be filled with coal as required. The retorts, four of which are placed in a setting, are 25 feet in length, and have a considerable taper to facilitate the downward movement of the mass. The heating is effected by producer gas, which, with the secondary air, enters at the top, the mixed gases passing downwards, the temperature on the outside of the retorts being highest at the top and decreasing to the bottom of the retorts.

In the Glover-West system, Fig. 12, the discharge of the coke is effected in a different manner. At the bottom of the retort is placed a screw conveyor, the pitch of which is less than the angle of rest of the coke, and this is slowly rotated, thus effecting the gradual discharge of the coke into the chambers below, from which it is removed at suitable intervals. As the coke is removed from the bottom, the whole mass of the material in the retort moves downwards, leaving a space at the top which is at once filled from the small hopper at the top of each retort and closed at the top by a gas-tight valve, shutting it off from the main coal bunker above. The small hopper is filled with coal every few hours by opening the valve and allowing it to fill up from the main bunker. The retorts are from 20 to 23 feet in length, and tapered, eight being placed in a single setting. For the purposes of heating, the setting is divided into a number of sections by horizontal division walls, the three upper sections receiving the combined waste gases from the chambers below, and abstracting much heat from these before they pass to the chimney. The next six sections form the heating chambers proper, each receiving a separate supply of producer gas from the furnace, as well as a separate supply of secondary air, and by suitably regulating the supplies, the temperatures in the different sections can be adjusted to that found most suitable for the particular coals carbonised. In the lowest section, the secondary air is admitted on its way to the heating sections, and thereby cools the now carbonised coke passing through the retorts, so that this is discharged in a relatively cool condition, and requires no quenching, its heat being returned to the setting with the secondary air, effecting a considerable economy in the fuel consumption.

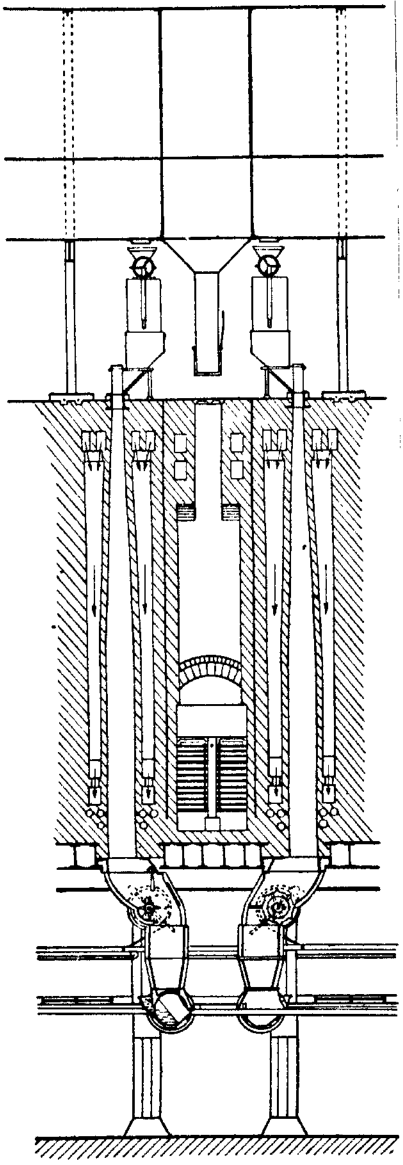

FIG. 11.

The constant movement of the mass through the retort in such continuous vertical retorts modifies the conditions of carbonisation to some extent. As with the intermittent retorts, the heat penetrates the mass of coal from the periphery and travels inwards, but the coal is constantly moving downwards, the uncarbonised coal takes the form of an inverted cone, the base of which is at the top, and the apex at a point about two-thirds of the length of the retort below. A small proportion of gas, with much steam, is formed on the inner and cooler side of the layer of decomposing coal, and escapes up through the core of uncarbonised coal, but with a caking coal the bulk of the gas is formed on the hotter outer portion of the decomposing pasty layer and passes up through the surrounding hot coke. Only a limited amount of free space is left at the top. The tar produced is thin and contains but little free carbon, no naphthalene trouble occurs with the gas after condensation, the carbon disulphide is reduced, and at the same time a high yield of gas of good calorific power is obtained. The coke formed from the continuous process is usually less dense than that obtained by intermittent carbonisation in vertical retorts.

Water-gas production in retorts. As already mentioned, admixture of blue water gas to the coal gas is being carried out to an increasing extent. In some instances the water gas is made in a separate plant and introduced into the coal gas stream at varying points, and in others the increased water-gas production is obtained by the addition of steam, to the retorts. Such steaming has been carried out in horizontal retorts by introducing steam below the coke mass throughout the length of the retort, and this has proved a valuable means of maintaining the gas supply during recent periods of coal shortage. The conditions in horizontal retorts are, however, not favourable to the manufacture of any considerable proportion of water gas in this manner, except with production of a high percentage of carbon dioxide in the mixed gas obtained. Vertical retorts, in which the steam has to pass through a much deeper bed of fuel, present much more favourable conditions, and it has long been the practice in the case of intermittent vertical retorts to admit steam to the bottom of the retort during the last 1–2 hours of the charge to increase the production of water gas, and recent requirements have brought about a great increase in the extent of this steaming.

With continuous vertical retorts, small amounts of steam have for a long time been admitted continuously at the bottom of the retort, resulting in the production of small amounts of water gas, and also in preventing ignition of the gas when the bottom doors are opened for the discharge of the coke. During recent years the extent of steam admitted (usually previously superheated) has greatly increased, and very considerable proportions of water gas are now being thus made in these retorts. The changes which occur are, however, not solely confined to the production of water gas, as secondary effects occur to the gas, tar, and ammonia production from the coal itself. This arises from the fact that owing to the increased production, the gases formed in the retort from the coal are thereby driven out of

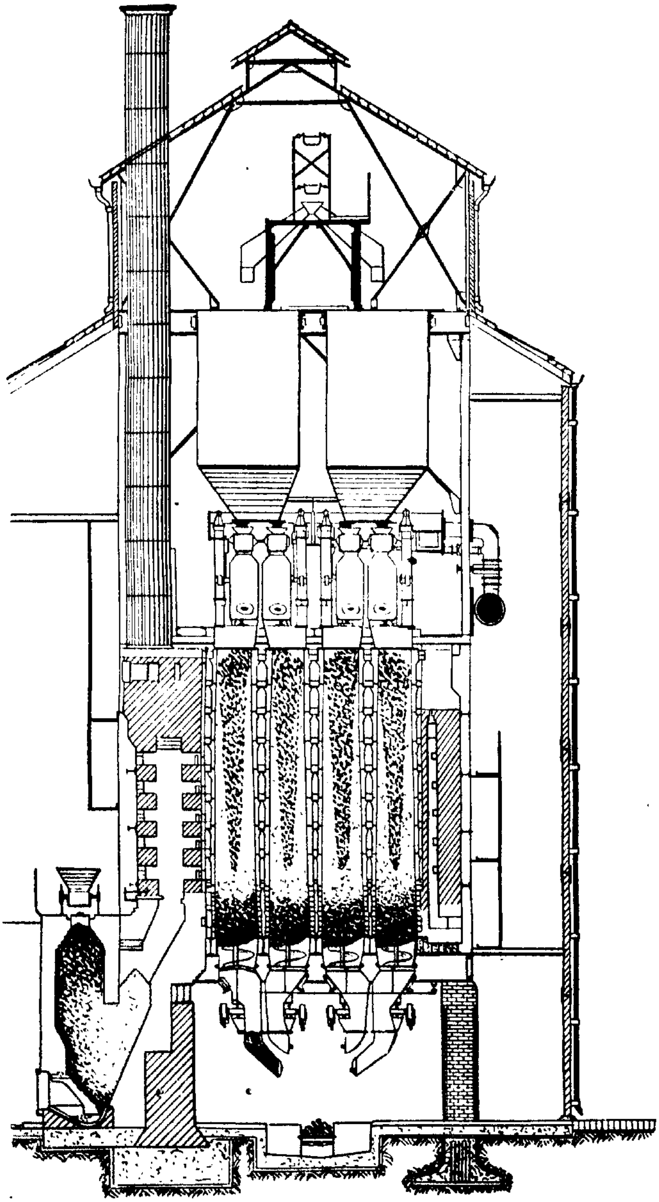

Fig. 12.

the retort more quickly, and thus exposed for a shorter time to the action of heat, which results in an increased yield of both tar and ammonia from the lessened decomposition occurring. The increased amount of hydrogen in the gas also tends to the production of tar containing a higher proportion of hydrogen. On the other hand, as the water-gas production is endothermic, a greater amount of fuel has to be used to maintain the temperature, and to obtain a low percentage of carbon dioxide in the gas high temperatures must be maintained at the lower portion of the retort; the coke yield is also slightly reduced by reason of the carbon used for water-gas production, and the percentage of ash in the coke obtained slightly increased. The amount of steam which can be added varies greatly with different classes of coal, but with certain kinds of coal, yields of 25,000 of mixed gas having a calorific power of 400 B.Th.U. have been obtained

Detailed investigations of the process of steaming in continuous vertical retorts have been made by the Investigation Committee of the Institution of Gas Engineers, and by the Fuel Research Board. (Gas Journ. 1920, 150, 640; 1921, 154, 542, 607.)

Carbonisation in larger bulk. Considerable attention has recently been paid, especially in Germany, to the carbonisation of coal for gas-making purposes in much larger bulk than the gas retort, and more in accordance with the practice where metallurgical coke is the product primarily required (*see* art. COKE). In this industry, as the gas is a by-product, the latter is employed for heating the ovens, but as with good working only about half the gas made is required for this purpose, a considerable surplus remains, which is generally used for boiler firing or in gas engines. In the north of England, a considerable amount of this surplus gas is either distributed in the neighbourhood of the ovens for general purposes, or more frequently the gas is sold in bulk to neighbouring gas undertakings, and mixed by them with the gas manufactured by their own plant. Middlesborough is almost entirely supplied with gas from coke ovens, and a material proportion of the supply of Leeds, Sheffield, and other towns is derived from the same source. In Germany and in the United States an increasing amount of coke-oven gas is employed in this manner.

In the coke-oven industry, the object aimed at is not only the production of coke, but also the utilisation of the slack inevitably produced in the operation of mining. This is in many cases first washed to remove mineral impurities as far as possible, and, when charged into the ovens, lies in a dense mass, which may be 10 tons or more in weight, and has very small interstitial spaces, and is sometimes further specially compressed; moreover, it contains 10 p.c. or more of moisture. Whilst the result of these alterations in the conditions from those in gas retorts effects an improvement in the quality of the coke produced, the gas, as it is formed, has greater difficulty in escaping from the centre of the charge, and the volume produced is usually lower, although it is of good calorific power, provided due precautions are taken to prevent the drawing in of undue amounts of furnace gases or air. The rate of carbonisation is also naturally much slower, as the larger the bulk in which the coal is charged the smaller is the *ratio* of heating surface per unit weight of coal, which further influences, to some extent, the composition of the resulting gas.

In Germany, particularly during the past few years, extensive experiments have been made with carbonising chambers of rather smaller size than coke ovens, holding from 3 to 6 tons per charge, in which the heating is effected by producer gas manufactured from the coke, and ordinary gas coal is carbonised instead of washed slack. In some of the forms adopted, horizontal chambers are used, and in others, these are provided with a sloping bottom, to facilitate the charging of the coal and discharge of the coke (*see* J. Gas Lighting, 1909, 106, 832). The coke obtained with such chambers is more closely allied to metallurgical coke than to ordinary gas coke, but where ordinary gas coal is used, the results, so far as quality of gas, tar, and ammonia are concerned, do not appear to differ materially from those obtained with intermittent vertical retorts. The relative advantages of such chambers and retorts lie more in connection with questions of the capital and working costs, of the desirability of such large carbonising units for making a uniform quality of gas, for adjusting the gas output to the seasonal variation in the demand for a public supply of gas, and of the suitability of the quality of coke produced to supply the local demand. Since 1911 a few installations of this intermediate type of chambers, between the size of retorts and coke ovens, have been adopted in this country.

The possibility of supplying gas of low calorific power has resulted also in the development of plants for the total gasification of coal, the general principle of which lies in the combination of a vertical retort with a water-gas or mixed gas producer, the coal passing into the producer through the former in which, partly by external heat and partly by the sensible heat of the hot water gas or producer gas passing through it, this is converted into a low-temperature coke before reaching the producer, where it is finally gasified, the mixed gas thus produced having a calorific power of 300–350 B.Th.U. Such plants have been adopted in many gas works in this country as auxiliaries, and also to a considerable extent on the Continent, but detailed and checked reports of their efficiency have not yet been published.

The efficiency of plants of this type would be very largely increased if oxygen were available at a cheap enough rate to be introduced along with steam instead of air into the producer. This matter is fully discussed by Hodsman and Cobb (Gas Journ. 1920, 150, 640).

CONDENSATION OF THE HOT GAS.

The volatile products driven off from the coal issue from the retorts into the mouthpiece, at a high temperature, which may, at times, reach 700°–800°, but this falls very rapidly as the gas passes up the ascension pipe. This arises partly from the fact that the difference in temperature between the gas within and the air circulating around the pipe is very great, and partly because the number of heat units to be

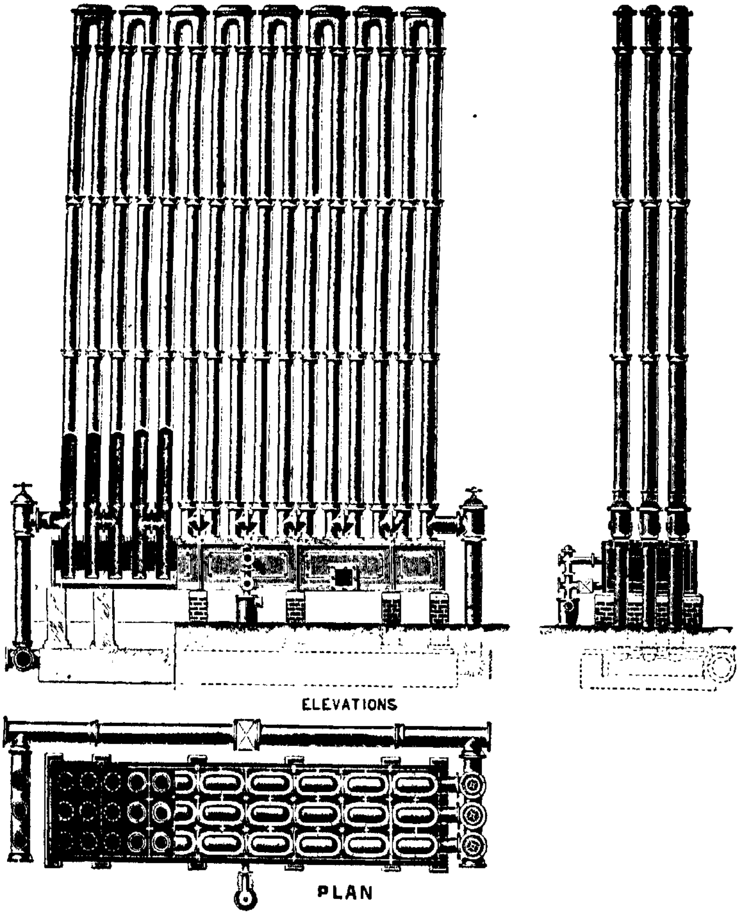

Fig. 13.

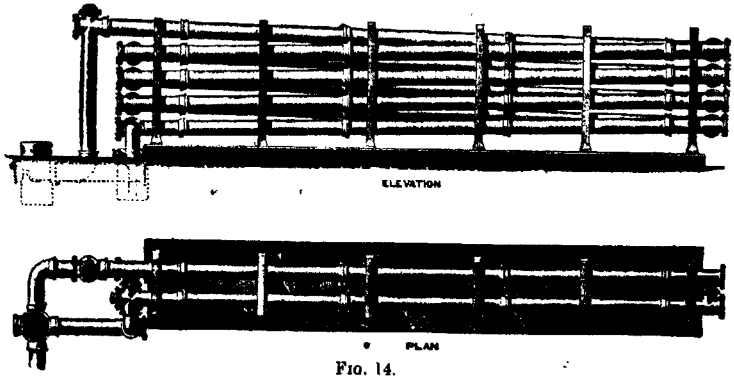

Fig. 14.

removed for a given temperature interval is relatively small, being due to the specific heat of the gases, and the latent heat of the tar vapours which condense, both of which are comparatively low. The temperature, therefore, falls rapidly up to the point at which water commences to condense, which is usually about 75°–80°, and from this point onwards the rate of cooling becomes very slow, chiefly owing to the high latent heat of the steam present. The dew-point is mostly attained by the time the gas reaches the dip pipe, and the temperature of the gas in the hydraulic or dry main, where the streams of gas from the different retorts mix, averages about 60°. By the time the steam commences to condense, by far the greater part of the tar vapours present have liquefied, and, owing to the rapid rate of cooling, these separate in the form of finely divided drops or vesicles, which are carried along with the stream of uncondensed gas mechanically in the form of a dense brown fog. In passing through the hydraulic or dry main, the greater part of this fog (generally from 70 to 80 p.c.) coalesces to form liquid tar, a considerable amount of water also separating here also, which combines with the ammonia and other impurities of the gas, forming ammoniacal liquor, these two liquids being removed in the manner already described. The combined streams from all the collecting mains of the separate setting unite in a trunk main termed the 'foul' main, by which they are conveyed from the retort house to the condensing plant proper, the combined stream having at this point a temperature of 50°–60°, and still containing much suspended tar fog, amounting in some cases to as much as one-third of the total tar production.

The cooling of the gases to approximately atmospheric temperature is effected by means of either atmospheric condensers or water-cooled condensers. Although many types of the former, differing in external appearance, are in use, the arrangement is in all cases such that the gas is passed slowly through apparatus exposing a large surface to the air, whereby the sensible heat of the gases and the latent heat of the vapours is given up to the air passing over the surface. In the water-cooled condensers water is employed as the cooling medium in place of air. This type of condenser requires a much smaller cooling surface than the atmospheric type, and the temperature to which the gas is cooled can be more readily regulated by controlling the flow of water, provided a sufficient supply of cold water is always available.

Fig. 13 shows the general arrangement of a vertical, and Fig. 14 of a horizontal, atmospheric pipe condenser, the manner of working being readily apparent from the diagram. Fig. 15 gives one section of an annular atmospheric condenser, in which the gas passes through the annular space between the inner and outer pipes, the air circulating not only over the outer pipe, but also ascending up the inner pipe, cooling both surfaces of the annular chambers. The volume of air passing up the inner pipe can be varied by means of the damper shown, and the extent of cooling of the gas regulated to some extent in this way. Fig. 16 gives a vertical and cross section of a water-cooled tubular condenser, the gas passing downwards over the outer surface of the small pipes, the water travelling up the pipes in the reverse direction to the gas stream, so that the gas leaving the apparatus is finally cooled by the incoming cold water. Many other good forms of both atmospheric and water condensers are in use, but their action is, in general, similar to those described.

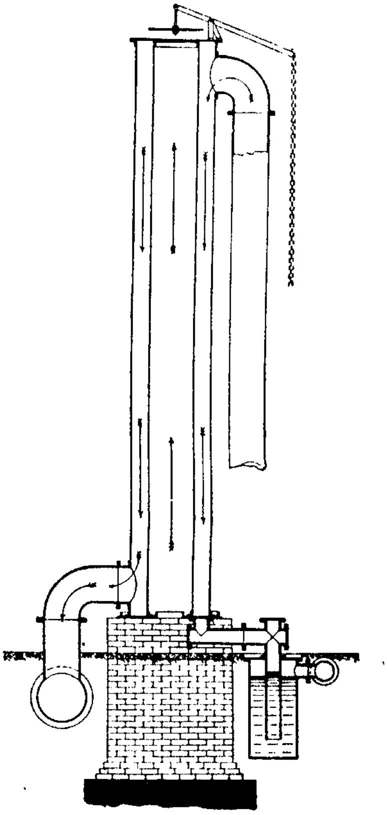

FIG. 15.

When high carbonising temperatures are employed, especially with certain classes of coal, the tar separating in the cold end of the condenser is apt to become semi-solid from crystallisation of naphthalene, eventually causing a stoppage. To avoid this it is convenient to arrange the connections and valves in such a manner that the inlet and outlet can be reversed; the previously cold end then receives the hot gas, and the thick tar becomes fluid and flows to the tar well, so that by periodic reversals of the stream blocks from this cause can be largely avoided.

In this country, where the seasonal changes in temperature are not, as a rule, very extreme, atmospheric condensers are employed to the largest extent, water condensers being employed

frequently in addition to effect the final cooling of the gas. On the Continent, where lower temperatures often prevail in winter and higher in summer, water condensers are more frequently used, and are enclosed in buildings to protect them from extremes of temperature.

In the early days of the manufacture, the only point considered was the simple cooling of the gas, but it was soon found that the manner in which the cooling takes place and the temperature to which the condensed tar is cooled in contact with the gas has a very material effect on the illuminating power of the gas produced. This arises from the fact that the illuminating power of the gas is very largely dependent upon the amount of benzene vapour present in it, and the lower the temperature to which the tar is cooled when in contact with the gas, the greater is the proportion of the benzene retained by the tar and the lower that left in the gas. The object aimed at in condensation is, therefore, not merely to cool the gas, but to carry out the cooling in such a manner as to leave in it the maximum amount of benzene vapour that it can retain at the lowest temperature to which it may be subsequently exposed during distribution, and, at the same time, to remove as completely as possible the vapours of higher-boiling substances, especially naphthalene. The importance of the removal of the latter arises from the fact that it is a solid at the ordinary temperature, and, when present, is liable to be deposited in crystals as the gas cools, and then causes blocks in the subsequent manufacturing plant and in the distribution system, causing great inconvenience. Although the amount of naphthalene in the gas sent out from the works rarely exceeds 15–20 grains per 100 cub. ft., and is usually much less, the deposited naphthalene may, when weather conditions are favourable to its separation, cause the stoppage of hundreds of service pipes in a single night in a large town.

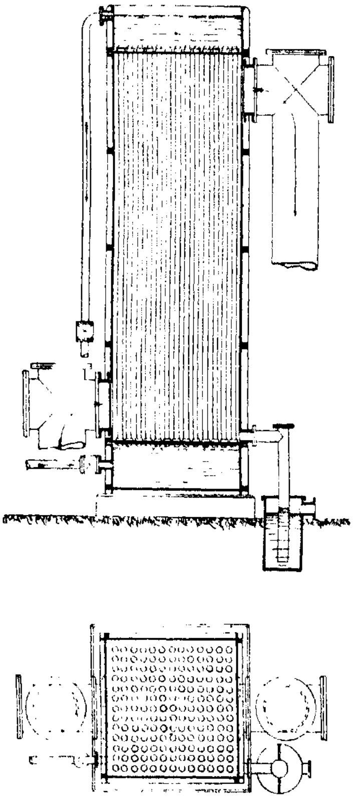

Fig. 16.

To effect the maximum retention of the lowest boiling-tar constituent, benzene, and the most complete removal of the higher-boiling constituents, the ideal procedure would be to arrange the condensing system so that the whole of the products of condensation flowed back in the opposite direction to the gas, whereby the gas is continually exposed to the solvent action of the liquids condensed from it at a lower temperature, in exactly the same manner as the vapours from a mixture of liquids are treated in a fractionating column in the process of fractional distillation. This principle is, however, very difficult of application in its entirety in the coal-gas manufacture, for many reasons. In the first place, as already mentioned, the separate streams from each retort undergo such rapid cooling before they combine to a single stream, that the tar has largely separated as a fog, which is inevitably largely carried forward mechanically with the gas, instead of travelling in the reverse direction; and, secondly, water also condenses from the gas, and as this does not mix with, and is specifically lighter than, the tar, it tends to cover the surface of the separated tar, and prevent the latter exerting its full solvent action on the substances still present as vapours in the gas. Where the coal is carbonised in larger units, as in coke ovens, the combined streams from the different ovens have a much higher temperature; here a strictly counter-current process is more possible, and Feld has patented a process for the treatment of such gas in a series of mechanical washers, in which the gas is successively washed with the products condensing at a lower temperature, the tar being obtained direct from these in different fractions, corresponding to those obtained in the first distillation of coal tar, and free from water, as the temperature is not allowed to fall to the point at which steam commences to condense (Eng. Pat. 26262, 1905; 20139, 1907; 27567–8, 1907; 9086, 1910). The removal of tar fog from the hot gas from coke ovens at temperatures above the dew-point is also carried out by the Otto process (*see* art. Coke).

The adoption of the counter-current system in gas works in the later stages of condensation, tends to have a beneficial effect, but the extent is only slight, owing to the above-mentioned protective effect of the condensed ammoniacal liquor, the quantity of which is much greater than that of the tar after the gas leaves the hydraulic main. In general, the widest divergence occurs in practice as to the manner in which the condensed tar is allowed to flow, this being sometimes with and sometimes against the gas streams, and sometimes alternately in each direction. It is, however, generally agreed that the tar which separates at the earliest stages, namely, in the hydraulic main, should be removed from contact with the gas before the temperature of the latter is reduced below 30°-35°.

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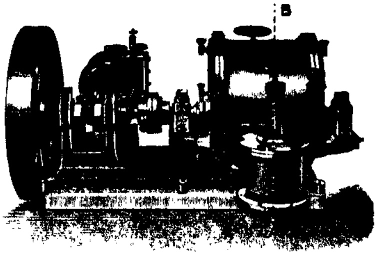

FIG. 17.

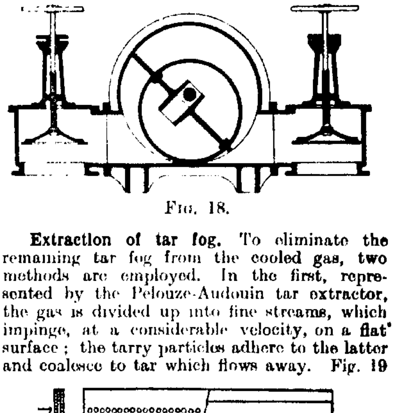

FIG. 18.

Extraction of tar fog. To eliminate the remaining tar fog from the cooled gas, two methods are employed. In the first, represented by the Pelouze-Audouin tar extractor, the gas is divided up into fine streams, which impinge, at a considerable velocity, on a flat surface; the tarry particles adhere to the latter and coalesce to tar which flows away. Fig. 19 shows the essential portion of the apparatus, which consists in two plates with a small space between them, the first of which is perforated with fine holes about $\frac{1}{20}$ inch in diameter, and the second with slots, the plates being so fixed that the gas issuing through the small holes impinges on the unperforated portion of the slotted plate. Two such pairs of plates are used in series, and these are arranged to form a bell (Fig. 20), which is sealed in the tar formed, and counterbalanced by weights so that it is free to

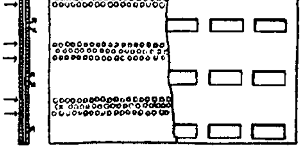

FIG. 19.

rise in the tar. If the amount of gas passing through the apparatus increases, the pressure within the bell tends to increase also, and the latter rises, and thus presents a larger number of holes for the gas to pass through, and *vice versâ*, and in this manner the velocity of the gas through the holes is kept approximately constant with varying production of gas. This apparatus is very efficient when properly worked, but is preferably maintained at a temperature of about 30°, as otherwise the deposited tar may become so thick that it cannot flow away, and the apparatus becomes blocked.

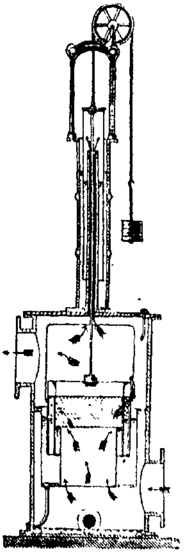

FIG. 20.

The second method consists in dividing the gas into a number of small streams, and bubbling these through ammoniacal liquor, thus serving the double purpose of removing tar fog, and of strengthening the weak liquor produced in other parts of the process (such as the retort-house liquor, or the liquor from the final scrubbers), which is fed into the apparatus. A very efficient apparatus of this type is the Livesey washer, the essential feature of which is shown in Fig. 21. It consists of a parallel series of troughs arranged in a cast-iron rectangular vessel, the lower portions of which are perforated with holes $\frac{1}{20}$ inch in diameter, as shown, this portion being sealed in ammoniacal liquor. The gas entering at the top passes down between the troughs, and forces some of the liquor through the holes into the interior of the troughs, thus unsealing the holes, through which the gas then bubbles, as well as through the second perforated plate across the width of the trough. The liquor in the trough is broken up into foam, and effects the removal of the tar fog and some ammonia from the gas, the washed gas passing away through the open end of the trough to the gas outlet. With proper working the amount of tar fog can be reduced to below 10 grains per 100 cub. ft., but the amount of ammonia removed varies greatly according to the strength of the liquor used, and the amount passed through the washer. Small amounts of carbon dioxide, sulphuretted hydrogen, and hydrocyanic acid are also removed by the washer.

Wet purification. To effect the complete, or almost complete, removal of ammonia, the gas is next washed with water in suitable apparatus, the washing being conducted on the counter-current principle, the gas meeting a current of water flowing in the opposite direction, so that the liquor leaving the apparatus meets with the gas richest in ammonia, and is thereby worked up to the highest strength possible, whilst the gas leaving the apparatus comes in contact with fresh water, containing little or no dissolved ammonia, and is thereby freed as completely as practicable from it. One of the oldest forms of apparatus for the purpose, which is still largely in use, is the *tower scrubber* (Fig. 22). This consists of a vertical tower of circular section filled with coke, flints, wooden boards on edge, or other material which exposes a large surface to the gas passing through it. Water is mechanically sprayed over the whole of the upper surface of the filling material, and slowly percolates

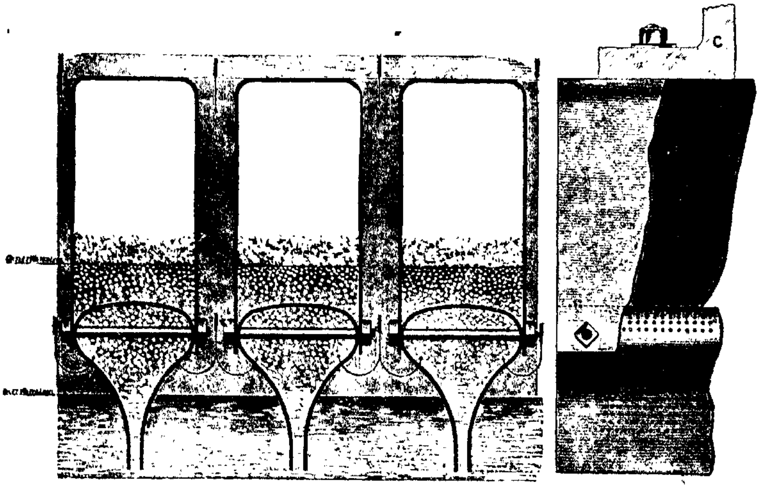

FIG. 21.

divergence occurs in practice as to the manner in which the condensed tar is allowed to flow, this being sometimes with and sometimes against the gas streams, and sometimes alternately in each direction. It is, however, generally agreed that the tar which separates at the earliest stages, namely, in the hydraulic main, should be removed from contact with the gas before the temperature of the latter is reduced below 30°-35°.

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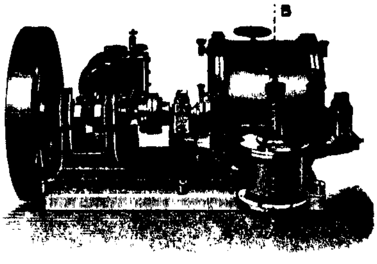
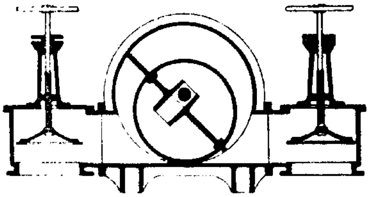


FIG. 17.



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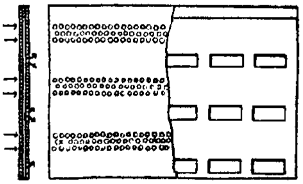

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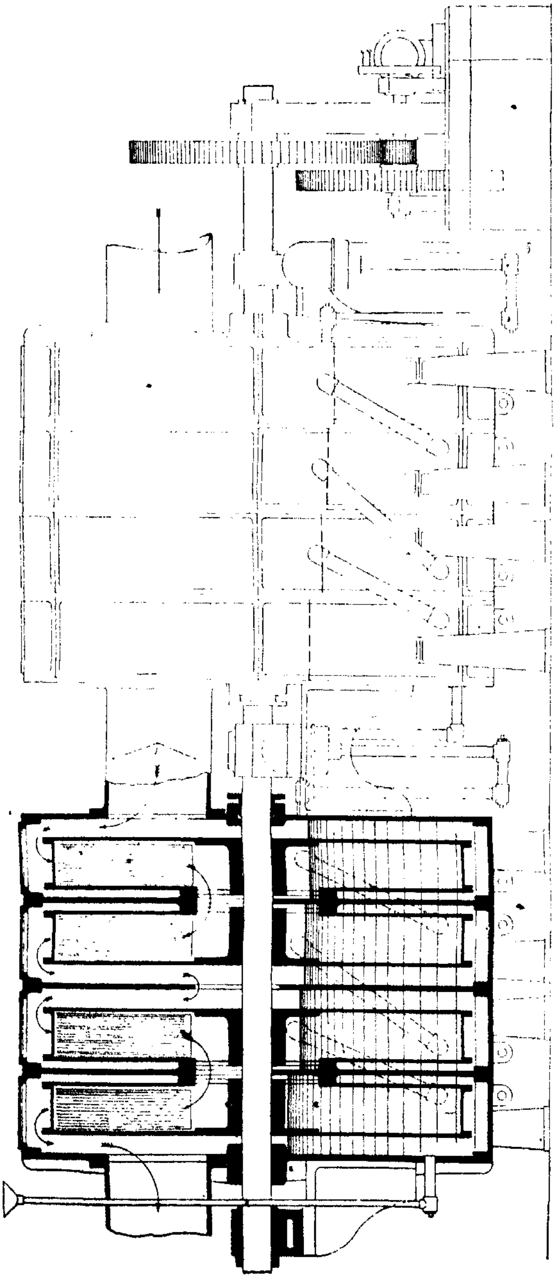

FIG. 23.

Naphthalene removal. Mention has already been made of the difficulty which arises from blockages both in the plant and mains on the works and on the mains and services in the district of supply, from the deposition of solid naphthalene from the gas. In the early days of the industry, when lower carbonisation temperatures were employed, no difficulty was experienced in this respect, as, although considerable amounts of naphthalene were even then present in the hot gas, the amount of other tar constituents boiling at the same or a lower temperature than naphthalene was sufficient to effect a practically complete washing out of the naphthalene from the gas in the ordinary process of condensation. As carbonising temperature increased, trouble from naphthalene became more and more noticeable, at first only where coals from the Durham coalfield were carbonised, but eventually, with still higher carbonising temperatures, from all classes of coal, and very serious nuisance from naphthalene stoppages took place, both manufacturers and consumers being affected.

The difficulty arises from the fact already discussed, that increased carbonising temperatures, when there is also a considerable free space above the coal in the retort, effect an increase in the production of naphthalene and a decrease in the production of lower-boiling tar oils, the proportion of the latter being then insufficient to effect the complete washing out of the naphthalene from the gas at the divergence occurs in practice as to the manner in which the condensed tar is allowed to flow, this being sometimes with and sometimes against the gas streams, and sometimes alternately in each direction. It is, however, generally agreed that the tar which separates at the earliest stages, namely, in the hydraulic main, should be removed from contact with the gas before the temperature of the latter is reduced below 30°–35°.

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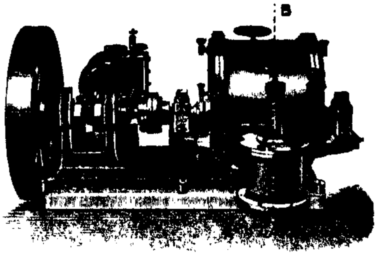

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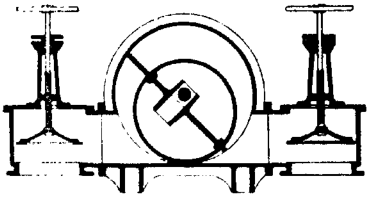

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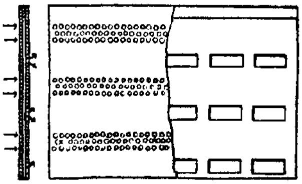


FIG. 19.

found in the purified gas to any very considerable extent. In some undertakings the hydrocyanic acid is extracted at an earlier stage by special processes in order to obtain cyanogen compounds in marketable form, and the methods employed for this purpose will be described later.

Where sulphuretted hydrogen alone is to be removed, the purifying material employed is moist hydrated ferric oxide, the naturally occurring bog iron ore being largely used for the purpose. This contains a sufficient amount of fibrous organic matter to render the mass porous and allow of the passage of the gas through it. Where artificial or natural ferric hydroxides, free from organic matter, are employed, these are mixed with material such as sawdust or wood chips to give the required porosity.

The material is charged in even layers into rectangular cast-iron vessels (Fig 24) containing wooden grids to carry the oxide, the thickness and number of the layers varying according to the size of the purifier The latter is then closed by a lid, which, in the diagram shown, is rendered gas-tight by the provision of vertical sides which drop into a water lute cast around the periphery of the purifier; so long as the pressure of the gas within the box does not exceed that equal to the depth of the water seal, no gas can escape. As, however, serious explosions have occurred owing to escape of gas through the water seal, owing to excessive pressure, the present tendency is to the adoption of luteless lids which are bolted to the purifier and made gas-tight by the insertion of a rubber joint between the purifier and cover.

The purifiers are mostly worked in sets of four, the connections being so arranged that the gas can be allowed to enter any box, and then pass in series through the remaining boxes. Frequently only three boxes are worked in series, the fourth being off for changing the material, or kept in reserve when freshly charged until sulphuretted hydrogen is found to be getting forward nearly to the outlet of the box before it, when the fresh box is put to work, and the first box in the series shut out and recharged with fresh oxide.

The sulphuretted hydrogen acts on the hydrated ferric oxide in two different ways, forming either ferric sulphide or a mixture of ferrous sulphide and free sulphur:

(1) $Fe_2O_3, xH_2O + 3H_2S = Fe_2S_3 + (x+3)H_2O$
(2) $Fe_2O_3, xH_2O + 3H_2S = 2FeS + S + (x+3)H_2O$

In neutral or faintly acid condition, the reaction takes place according to the second equation, but in slightly alkaline condition ferric sulphide alone is formed, and as the coal gas entering the purifiers always contains traces of ammonia, it is this compound which is chiefly formed in the gas purifiers.

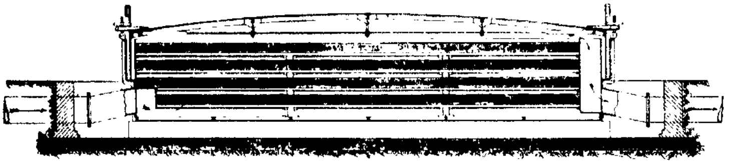


FIG. 24.

When the mass has ceased to absorb sulphuretted hydrogen, it is removed from the purifier and spread out on the floor in moist condition, with occasional turning over, to expose it to the air, when the ferric sulphide is oxidised, reforming hydrated ferric oxide, with separation of free sulphur. As soon as this reaction is complete, the mass can be returned to the purifier for the extraction of further amounts of sulphuretted hydrogen, this alternate process of fouling and revivification being continued until the mass contains 50–70 p.c. of sulphur, when it is sold for its sulphur content, being chiefly used for sulphuric acid manufacture, one advantage of the material for this purpose being its almost complete freedom from arsenic.

As the crude gas entering the purifiers always contains some oxygen, the revivification of the ferric sulphide to ferric oxide and sulphur always takes place to some extent in the purifier itself, and the length of time for which a purifier will run without changing depends, to a large extent, on the amount of oxygen in the crude gas. All things considered, the volume of oxygen most suitable is rather more than half the percentage volume of the sulphuretted hydrogen in the crude gas; and where the air accidentally getting in to the gas does not reach this amount, more is added. A still larger addition of air further increases the time the purifiers will run without changing, and consequently the cost for labour, but the extra amount of oxygen and nitrogen remaining in the gas lowers its quality, and if too much oxygen is present the separated sulphur may even fire in the boxes, and, apart from the damage caused in the box, the gas may be badly contaminated with sulphur dioxide. The temperature of the gas passing through the purifiers should not fall below about 15°, as then the action of the oxygen becomes very slow.

Instead of working the rotation of the purifiers in the manner mentioned above, which was formerly universal, modified methods are now frequently adopted. Thus, for example, instead of putting on a fresh box as the last in the series, it is now frequently put on as the first box, where it removes practically the whole of the sulphuretted hydrogen, and the gas coming from the outlet of the two boxes last in the series becomes quite free from sulphuretted hydrogen in a short time, any sulphuretted hydrogen passing from the last purifier during this period being taken up by a 'catch' purifier placed on the common outlet main. At intervals of 24 or 48 hours or more, the last box is made the first box of the series, when the same change divergence occurs in practice as to the manner in which the condensed tar is allowed to flow, this being sometimes with and sometimes against the gas streams, and sometimes alternately in each direction. It is, however, generally agreed that the tar which separates at the earliest stages, namely, in the hydraulic main, should be removed from contact with the gas before the temperature of the latter is reduced below 30°–35°.

Formerly, when gas of higher illuminating power was made, it was generally regarded as important that the cooling of the gas, at any rate from 60° to about 25°, should take place slowly, if loss of illuminating power was to be avoided. With gas of the quality now usually made, this is, however, of but little influence, rapid cooling in this case effecting but little reduction of the calorific power, provided the temperature is not reduced below 15°–20°; if, however, the gas is at any time cooled in presence of tar much below 15°, decided reduction in calorific power occurs, and too great reduction of temperature in condensation is, therefore, always to be avoided.

During the whole of condensation, including that occurring in the retort house, from 9 to 15 gallons of tar per ton of coal (varying with the nature of the latter and the temperature and method of carbonisation) are separated from the gas, together with a quantity of ammoniacal liquor varying usually from about 10–15 gallons per ton. These both flow together to the well or wells, to which any tar and liquor from the subsequent apparatus also gravitate. The condensed water removes a large proportion of the ammonia from the crude gas (usually about half of the 400–450 grains per 100 cub. ft. contained in the gas issuing from the retorts), and the alkaline ammonia solution also extracts the whole of the hydrochloric acid in the gas formed from the chlorine in the coal, and some of the carbon dioxide, sulphuretted hydrogen, and hydrocyanic acid. The liquor obtained in condensation is termed 'virgin liquor,' that portion formed in the retort house being usually, though not invariably, weak, and containing from 0·5 to 1·5 p.c. of ammonia, whilst that from the condensers is more concentrated, and may contain 4 p.c. or more. The cooled gas mostly contains some 200 grains of ammonia, and 50–100 grains of hydrocyanic acid per 100 cub. ft., from 1 to 2 p.c. of sulphuretted hydrogen, and 1–3 p.c. of carbon dioxide, and in addition also an appreciable amount of tar fog, which has not been removed from the gas in its passage through the condensers, and which, if not previously eliminated, is deposited in the subsequent purifying apparatus, rendering them much less efficient.

Exhausters. The gas pumps, or exhausters, are in the most usual practice placed at the outlet of the condensers, the gas being drawn through the condensers and forced on through the subsequent plant. Various kinds of exhausters are employed, the most popular being those of the Beale rotary type, shown in Figs. 17 and 18. These are automatically controlled by the vacuum in the hydraulic main so as to maintain the latter constant, a service pipe being run from the hydraulic main to a governor in the exhauster house. The latter governor is then connected with a throttle valve controlling the steam supply to the exhauster, so that the speed at which the latter runs is automatically regulated to give a steady vacuum; or the latter may be run at a constant speed, and the governor connected to a valve on a by-pass main from the inlet to the outlet of the exhauster, allowing more or less gas to flow back from the exhauster outlet to the inlet, according as the rate at which the gas is evolved from the retort falls or rises.

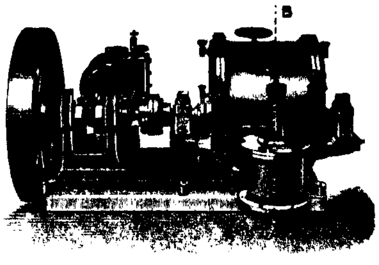


Fig. 17.

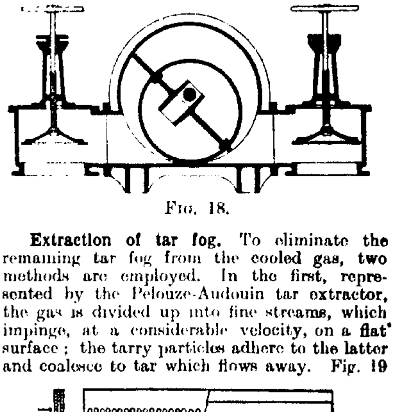


Fig. 18.

Extraction of tar fog. To eliminate the remaining tar fog from the cooled gas, two methods are employed. In the first, represented by the Pelouze-Audouin tar extractor, the gas is divided up into fine streams, which impinge, at a considerable velocity, on a flat surface; the tarry particles adhere to the latter and coalesce to tar which flows away. Fig. 19 shows the essential portion of the apparatus, which consists in two plates with a small space between them, the first of which is perforated with fine holes about $\frac{1}{20}$ inch in diameter, and the second with slots, the plates being so fixed that the gas issuing through the small holes impinges on the unperforated portion of the slotted plate. Two such pairs of plates are used in series, and these are arranged to form a ball (Fig. 20), which is sealed in the tar formed, and counterbalanced by weights so that it is free to

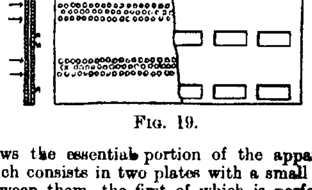


Fig. 19.

but calcium hydrosulphide, and, indeed, all the soluble hydrosulphides, when free from polysulphides, combine very slowly, if at all, with carbon disulphide in absence of oxygen. Veley (Chem. Soc. Trans. 1885, 47, 478) suggests that the active compound is calcium hydroxyhydrosulphide Ca(OH)(SH), but the writer regards it as much more probable that the real absorbent is calcium disulphide CaS_2, formed from the hydrosulphide by oxidation:

$$Ca(SH)_2+O=CaS_2+H_2O$$

for although the pure sulphides and hydrosulphides of potassium, sodium, ammonium, and calcium scarcely unite with carbon disulphide at the ordinary temperature, the disulphides of the above metals in all cases combine rapidly and completely with it, forming *perthiocarbonates*, such as Na_2CS_4 (Gélis, Compt. rend 81, 282; Yeoman, Chem. Soc. Trans. 1921, 119, 38). This supposition explains why some oxygen is necessary for carbon disulphide absorption, as it is required to effect the formation of polysulphide from the primary hydrosulphide, whilst excess of oxygen oxidises the latter to thiosulphate, &c.

Apart from the objections to the process already mentioned, it will be seen that this method involves the complete removal of carbon dioxide from the gas, whether this is otherwise advisable or not, and an economical process which does not necessitate the simultaneous removal of the carbon dioxide is very desirable. Many unsuccessful attempts have been made to devise such a process Thus Claus (J. Soc Chem. Ind 1887, 6, 27; Eng. Pats. 7585, 1886; 3627, 1887) showed that a solution of ammonium polysulphide removed carbon bisulphide, and this has been confirmed by others, but it has hitherto been found that the absorption is not regular, varying from time to time for reasons which have not yet been elucidated. The first action is probably the formation of a solution of ammonium perthiocarbonate $(NH_4)_2CS_4$, but this is exceedingly unstable, and readily decomposes, giving off CS_2. It is, however, capable of undergoing another change, yielding ammonium thiocyanate

$$(NH_4)_2CS_4=NH_4CNS+2H_2S+S$$

and if the conditions under which this change takes place quickly and with certainty could be ascertained, and economically maintained, this should form a cheap process for the purpose.

The Cooper liming process (Eng. Pat. 5713, 1882), in which small quantities of lime are added to the coal before carbonisation, although primarily intended to increase the yield of ammonia, also effects a reduction in the amount of carbon disulphide; but the large-scale experiments with the process made about thirty years ago were abandoned, chiefly on account of the deterioration in the quality of the coke produced. Paterson & Twycross (Eng. Pat. 26772, 1910) have introduced a modified method, whereby a regulated amount of powdered lime is distributed evenly over the surface of the coal on its way to the retort, the powder being made to adhere by the action of a small jet of steam. The process has been at work for some years at the Cheltenham Gas Works, using about 2 per cent. of lime, and has not resulted in any material deterioration of the coke, and has given an increased yield c ammonia, whilst the amount of sulphur othe than sulphuretted hydrogen in the gas ha averaged 20 grains per 100 cub. ft., as compared with more than double this amoun when the liming is omitted.

It has also long been known that by reheatin the gas freed from sulphuretted hydrogen t 300°–350° the carbon disulphide is largel converted into sulphuretted hydrogen, whic may then be removed by oxide of iron purification, but until recently practical difficulties i large-scale working prevented its adoptior (For a full account of those methods, *see* Carpenter, J Gas Lighting, 1914, 126, 928.) Th first successful plant of any magnitude fo carrying out the method was that of Hall an Papst at the Oregon Works, U.S.A., where plant was erected dealing with 4,000,000 cub. ft of gas per diem, and effected an average reduction of the sulphur from 58 to 17 grains pe 100 cub ft

As the result of several years' work th South Metropolitan Gas Co., have now worke out a successful and economical process for th complete removal of the carbon disulphide fror the gas depending on the passage of the ga heated to 450° over a catalyst (Carpenter, J Gas Lighting, 1914, 126, 928; Evans, J. Soc Chem Ind. 1915, 9) A number of metals, suc as iron, nickel, cobalt, and copper may b employed, but the most effective catalyst consists of porous fire-clay impregnated with nicke reduced from the chloride, and this is the on employed in practice, the carbon disulphid under the conditions named reacting with th hydrogen of the gas, yielding sulphurette hydrogen and carbon:

$$CS_2+2H_2=2H_2S+C$$

In carrying out the process, the gas freed fron sulphuretted hydrogen passes first through tubular heat interchanger, where it is heate by the hot gas coming from the catalysin tubes, and thence to a heating chamber i which are assembled the vertical 6-inch tube filled with the fire-clay-nickel catalyst, maintained at a temperature of 420°–440°. The gas with the carbon disulphide completely converte into sulphuretted hydrogen, passes through th heat interchangers, giving up a large portio of its heat to the incoming cold gas, and thence after complete cooling, to oxide of iron purifier for the removal of the sulphuretted hydrogen.

Apart from the conversion of the carbo disulphide into sulphuretted hydrogen an small amounts of hydrocyanic acid present int ammonia, no material change takes place i the composition of the gas, and its illuminatin and calorific powers are substantially unchanged The carbon deposited from the carbon disulphid accumulates on the catalyst, and is periodicall removed by careful burning in a regulate stream of air. No trouble from the 'poisoning of the catalyst has been experienced.

The process is now successfully at work a the different works of the South Metropolita Gas Co., the largest installation being capabl of dealing with 15,000,000 cub. ft. of gas pe diem, and reducing the sulphur to about grains per 100 cub. ft.

Guillet (J. Gas Lighting, 1912, 118, 986 passes the heated gas, freed from sulphuretted hydrogen, over heated ferric oxide, when the moisture in the gas reacts with the carbon disulphide forming sulphuretted hydrogen and carbon dioxide:

$$CS_2+2H_2O=2H_2S+CO_2$$

the sulphuretted hydrogen formed being absorbed by the ferric oxide.

Apart from the carbon disulphide, the gas always contains sulphur in the form of other organic sulphur compounds amounting to 4–10 grains per 100 cub. ft., which have not yet been successfully removed. A large proportion of this irremovable sulphur is in the form of thiophen, and, in addition, mercaptans and alkyl sulphides have been detected.

Removal and recovery of cyanogen compounds. It has long been known that crude coal gas contains cyanogen derivatives, and that their quantity tends to increase with increasing carbonising temperatures. The only compound of this kind that has been detected with certainty in the gas is hydrocyanic acid, although it is possible that cyanogen itself may be present in small quantity. The total amount varies considerably at different works, but with the temperatures at present mostly employed, the amount of hydrocyanic acid produced in the gas issuing from the retorts averages about 120–130 grains per 100 cub. ft., of which about one quarter is removed in the virgin liquor during condensation, partly as ammonium cyanide, but chiefly as ammonium thiocyanate, into which the cyanide formed also passes on storage. Smaller amounts are absorbed in a similar manner in the washers and scrubbers, but with high retort temperatures from 90–100 grains of hydrocyanic acid per 100 cub. ft. (equivalent to about 4–4·5 lbs. of crystallised sodium ferrocyanide $Na_4FeCy_6,10H_2O$ per ton of coal) usually remain in the gas entering the purifier.

Where lime alone is used for purification, the hydrocyanic acid is completely absorbed with the other impurities, and converted into calcium thiocyanate; and where ferric oxide is used, the greater quantity is likewise absorbed with formation of insoluble iron ferrocyanides and double ferrocyanides of iron and ammonium (crude Prussian blue) as well as ammonium thiocyanate. The more complete the removal of ammonia from the gas before the purifiers, the greater is the amount converted into ferrocyanide, and the smaller the production of thiocyanate.

The greatly increased demand for cyanide following on the introduction of the McArthur-Forrest cyanide process for extraction of gold from the mine 'tailings,' resulted in many attempts being made for the utilisation of the cyanogen compounds in the crude gas. At first the spent oxide was utilised for this purpose, being sold to chemical manufacturers for its Prussian-blue content, where this reached an amount of 6–8 p.c. A number of processes were also devised for the special recovery of the hydrocyanic acid by extracting it from the gas before the latter reached the purifier. In these processes the hydrocyanic acid is recovered either as (1) ferrocyanide or (2) thiocyanate. For the former, the gas is washed with a solution containing alkali and ferrous hydroxide, carbonate, or sulphide in suspension, which absorbs the hydrocyanic acid with production of the ferrocyanide of the alkali used, the reaction with ferrous sulphide and sodium carbonate, for example, being:

$$FeS+2Na_2CO_3+6HCy$$
$$=Na_4FeCy_6+H_2S+2H_2O+2CO_2$$

Where ammonia is used as the alkali, as in the processes of Rowland (Eng. Pat. 22347, 1891), Bueb (Eng. Pat. 9075, 1898), and Lessing (Eng. Pat. 2090, 1907), the gas is treated before the removal of ammonia in a suitable washer with a strong solution of ferrous sulphate, which is converted first into ferrous sulphide and ammonium sulphate by the sulphuretted hydrogen and ammonia of the crude gas, and then yields ammonium ferrocyanide. The latter solution is unstable, and to a large extent combines with the excess of iron present, yielding insoluble double ferrocyanides of iron and ammonium, the proportion of insoluble ferrocyanides produced increasing with increasing strength of the ferrous sulphate solution used. The sludge obtained, containing chiefly crude Prussian blue, with the excess of unused ferrous sulphide, is sold to chemical manufacturers for conversion into saleable ferrocyanide or cyanide.

Where a fixed alkali is used (soda and lime being the only ones available, on account of price), the gas is treated after the removal of ammonia in a washer fed with a mixture of sodium carbonate and ferrous carbonate (Knublauch, Eng. Pat. 15164, 1887), or a solution of ferrous sulphate with excess of lime, when the bulk of the hydrocyanic acid is absorbed and converted chiefly into the soluble sodium or calcium ferrocyanide, only small amounts being converted into insoluble ferrocyanides. The sodium ferrocyanide solution, after filtration from the excess of ferrous sulphide, &c., is directly evaporated and crystallised; the calcium ferrocyanide solution, on the other hand, is unstable when heated, and is preferably first converted into the sodium salt, by addition of the requisite quantity of sodium carbonate, or, if the potassium salt is required, the calcium ferrocyanide solution may be treated with potassium chloride solution, when the sparingly soluble calcium potassium ferrocyanide CaK_2FeCy_6 is precipitated, and after filtration may be converted into a pure solution of potassium ferrocyanide by addition of the requisite amount of potassium carbonate. In the Davis-Neill process (Eng. Pat. 26566, 1901), the treatment with sodium and ferrous carbonate is carried out before the removal of ammonia from the gas, and the liquor from the washer first distilled to recover ammonia.

In all these processes, a certain amount of hydrocyanic acid is converted into thiocyanate, the proportion formed being greater when ammonia is present, and *carbonyl ferrocyanides* are also usually produced to some extent. Carbonylferrocyanic acid $H_3Fe(CO)Cy_5$ may be regarded as ferrocyanic acid in which 1 molecule of HCy is replaced by the radical CO, the formation of these salts being doubtless due to the presence of carbon monoxide in the gas treated. They have little or no commercial value, and accumulate in the mother liquors, being very soluble in water.

For the recovery of the hydrocyanic acid as thiocyanate, according to the British Cyanide Co.'s process (Eng. Pat. 13653, 1901), the gas, whilst still containing ammonia, is passed through a washer containing water or ammoniacal liquor, to which free sulphur is periodically added. The ammonia and sulphuretted hydrogen dissolve in the water, forming ammonium sulphides, which dissolve the sulphur, yielding ammonium polysulphide solution, and the latter absorbs the hydrocyanic acid, forming ammonium thiocyanate So long as free sulphur is present, the formation of polysulphide and of thiocyanate continues, and a solution can be obtained containing from 3 to 5 lbs of ammonium thiocyanate per gallon. Except for volatile ammonium salts, such as sulphide, which are expelled on heating, the solution is comparatively pure, and is sold for conversion into cyanide. According to the modification of P. E. Williams (Eng. Pat. 23624, 1909), the gas, freed from tar-fog but containing ammonia, is passed through a purifier charged with spent oxide rich in sulphur, the latter supplying the necessary sulphur for the extraction. Water is periodically sprayed on to the upper surface of the spent oxide and drains to the bottom of the purifiers, and is converted during the passage into a concentrated solution of ammonium thiocyanate by the same series of reactions.

Other purification processes. As already mentioned, a portion of the sulphuretted hydrogen and carbon dioxide is removed along with the ammonia, the solution of the latter in water absorbing these acid gases with formation of ammonium sulphides and carbonates, but the amount of ammonia present is much below that required for their complete removal. Many attempts have been made to modify the scrubbing process in such a manner as to effect the complete removal of these two impurities. Hills (Eng. Pats. 1369, 1868; 934, 1874; 1895, 1875) showed that when the ammoniacal liquor is heated to about 90°, it gives off large quantities of carbon dioxide and sulphuretted hydrogen, but only small amounts of ammonia, the residual liquor then containing large amounts of free ammonia, which may be used for washing a further amount of the acid gases from crude gas. A modification of Hills' method has been described by Holgate (J. Gas Lighting, 1895, 65, 1133). Claus (Eng. Pats. 2838 and 2865, 1881; 4644, 1882; 5959, 1883) combined Hills' process with the continuous distillation of a large amount of liquor, the ammonia being returned to the gas, so that the amount of ammonia in the gas in the scrubbers was four or five times that normally present, and was enabled, on a moderate scale, to effect in this manner a complete removal of the sulphuretted hydrogen and carbon dioxide from the gas, doing away with the necessity for any further dry purification. By washing also with a solution of ammonium polysulphide, the amount of hydrocyanic acid and carbon disulphide was largely reduced. The mixed sulphuretted hydrogen and carbon dioxide evolved from the heated liquor were, after recovery of the ammonia present by washing with water or acid, mixed with just sufficient air to convert the sulphuretted hydrogen into sulphur and water, and passed through heated ferric oxide in the 'Claus kiln,' the sulphur produced being condensed in suitable chambers.

Great hopes were entertained as to the success of the process, but, unfortunately, the practical difficulties of working which manifested themselves when the process was tried on a larger scale have never been overcome, and at Belfast, where the process was tried for many years, it was not found possible regularly to effect complete removal of the sulphuretted hydrogen, and the loss of ammonia was very considerable (J. Gas Lighting, 1897, 69, 1475).

Processes are at present also on trial with the object of recovering the ammonia from the gas direct as sulphate by utilising the sulphuretted hydrogen of the crude gas as the source of the sulphuric acid. Various methods to attain this end have been patented by Burkheiser (Eng. Pats. 20920, 21763, 1908; 17359, 1910; 16172, 1912), and by Feld (Eng. Pats. 3061, 1909; 5838, 1911; 157, 10147, 1912; Zeitsch. angew. Chem. 1912, 705), but these processes are still in the experimental stage.

Yield of gas and by-products. The volume of gas obtained varies naturally to a considerable extent, according to the quality of the coal carbonised, to the conditions of carbonisation, and also to the extent to which the furnace gases, consisting chiefly of nitrogen, are drawn into the gas through the porous retorts. At the present day the volume of gas produced from a ton of coal, without steaming the retorts, measured moist at 60°F. and 30 inches bar., usually falls within the limits of 9000 and 13,000 cub. ft., and, except in small works, or where gas of high illuminating power is produced, the yield does not often fall below about 11,000 cub. ft. From the same classes of coal, the higher the yield of gas the lower is the illuminating power and calorific power, but, in general, the total yield of light represented by the multiple of make per ton × illuminating power, becomes higher as the make of gas increases, and this is the case to a still greater extent with the yield of heat units per ton of coal, as the calorific power falls off with increasing gas production to a much smaller extent than is the case with the illuminating power: and, in view of the fact that the heating value of the gas is now by far the most important factor, there is a constant endeavour to obtain as high a yield as possible.

The constituents present in purified coal gas obtained by the simple carbonisation of coal in more than minute quantity are carbon dioxide, ethylene, benzene, oxygen, carbon monoxide, methane, hydrogen, and nitrogen. Their relative proportions naturally vary considerably, but for the most part fall within the following limits:—

Carbon dioxide	0·0–3·0	p.c.
Ethylene	2·0–4·0	,,
Benzene	0·5–1·0	,,
Oxygen	0·0–1·5	,,
Carbon monoxide	4·0–15·0	,,
Methane	22·0–25·0	,,
Hydrogen	38·0–55·0	,,
Nitrogen	2·0–20·0	,,

The ethylene and benzene are usually estimated together and recorded as 'unsaturated hydrocarbons,' no very satisfactory quick method for their separate determination being available. In addition to methane, the richer coal gases contain small amounts of ethane, which is, however, also difficult of estimation in ordinary analyses. The nitrogen is usually taken as the difference between the sum of the other constituents and 100. The sp.gr. of coal gas falls mostly within the limits 0·4 and 0·55 (air = 1).

The yield of coal tar with horizontal and inclined retorts varies commonly from 9 to 13 gallons per ton of coal, averaging about 10 gallons, or some 5·5 p.c. of the weight of the original coal. Its sp.gr. varies from about 1·10 to 1·25, this depending largely on the temperature of carbonisation. The higher the temperature to which the volatile products are exposed, the higher is the average carbon percentage, and the lower the hydrogen percentage of the tar, and the greater the amount of the so-called 'free carbon' formed; the latter, although in appearance resembling amorphous carbon, always contains hydrogen, and consists of derivatives of very complex hydrocarbons, which are infusible and insoluble in the remaining tar. The yield of tar from vertical retorts is higher and is increased by steaming, the tar being much thinner, and having a sp.gr. of 1·07–1·13, and only contains 40–55 p.c. of pitch instead of the 60–70 p.c. in tar from horizontal retorts, and also only small amounts of 'free carbon.'

The ammoniacal liquor contains a quantity of ammonia calculated as sulphate, equivalent generally to a yield of from 22 to 30 lbs. of the latter per ton of coal, but is usually higher (up to 45 lbs.) in continuous vertical retorts, and is considerably increased by steaming. The composition of ammoniacal liquor and its working up into ammonium salts, are described in the article AMMONIA.

The yield of coke averages about 14 cwts. per ton of coal, but a considerable amount of this is used for heating the retort setting and other purposes on the works, so that the amount available for sale is much less than this, and a sale of 10 cwts. per ton is not often exceeded.

Manufacture of carburetted water gas. In order to obtain a gas of high illuminating power to mix with the gas from ordinary coal, and increase the illuminating power of the latter, cannel coal was formerly used, rich varieties of which give a gas of as high an illuminating power as 35 or even 40 candles. Owing to the increasing scarcity and cost of cannel, about 1890 recourse was had to oil, as a source of rich gas, this being either carbonised in retorts making oil gas of 60 candle power or higher, or used in the preparation of carburetted water gas, *i.e.* a mixture of water gas and oil gas, which during the previous 20 years had been largely manufactured in the United States, and had, to a large extent, displaced coal gas, and which can readily be made of 20–25 candle power. The carburetted water gas was adopted in a large number of cases, as this plant has the advantage that the volume of gas produced is much greater than with an oil-gas plant, and the apparatus, starting cold, can be put to work in a very short time, and forms a valuable means of quickly increasing the supply in times of sudden great consumption, such as are brought about by fogs or very cold weather. Owing to the now almost general reduction of illuminating power to a quality the ordinary gas coal is capable of yielding, the use of oil gas has been almost entirely given up, but carburetted water gas of a calorific power similar to that of the coal gas is made in many undertakings to a large extent, and mixed with the coal gas before storage, about 10 p.c. of the total gas made in the United Kingdom in 1913 consisting of this gas. As mentioned above, water gas alone is now also frequently admixed with the coal gas in many cases.

The manufacture of water gas itself (commonly known as 'blue' water gas, owing to its burning with a blue non-luminous flame) is dealt with in a separate article (*see* GAS, WATER), and will only be considered here so far as it concerns the manufacture of the carburetted gas. Fig. 25 shows the general arrangement of the Humphreys and Glasgow plant largely employed in the manufacture. The generator A is filled with coke, the latter being ignited at the bottom and raised to incandescence by blowing in air from a fan, the amount of air being regulated so that the gases coming away from the generator contain sufficient carbon monoxide to burn readily. These pass to the top of the 'carburettor' F, which is filled with fire-brick checker work, a secondary stream of air being added to the gas at the top, when the carbon monoxide burns and raises the fire-brick checker work to a red heat. The gases pass away from the bottom and enter the bottom of the 'superheater' G, where they meet with more air, and the remaining carbon monoxide burns to the dioxide, and raises the checker work in the superheater also to a red heat. The waste gases escape into the air from the 'stack-valve' on the top of the superheater, which is open during this operation. When the coke in the generator is sufficiently hot, and the checker work in the carburettor and superheater raised to the required temperature, all three air valves and the stack valve are closed, and steam turned on to the generator, water gas being produced, which passes to the top of the carburettor. At this point oil is sprayed into the gas, and passes with the latter over the hot checker work, and is first volatilised, the vapours then undergoing decomposition, which is completed in passing through the superheater, the oil being thus converted into permanent gas and condensible tar vapours. The stack valve being now closed, the mixed gas passes through a seal pot, H (which prevents gas returning up the stand pipe when the stack valve is open), thence through scrubbers filled with boards and tubular water-cooled condensers to reduce the gas to atmospheric temperature and condense the tar vapours and excess of steam from the gas. As the formation of water gas takes place with absorption of heat, the temperature of the coke in the generator steadily falls, and eventually reaches a point at which the amount of carbon dioxide produced becomes excessive, and the steam is then shut off, the oil having been also shut off from the carburettor a short time previously; the generator air valve is then again opened, and also the secondary air-valves and stack valve, and the coke and checker work raised to a suitable temperature as before, this period of working being known as the 'blow.' When this is effected, the air and stack valves are again closed, steam and oil turned on, and carburetted water gas made for a further period, known as the 'run,' until the temperature in the generator again falls too low, when steam and oil are again shut off and the blow recommenced. This sequence of operations is then maintained continuously, except during the intervals necessary for adding fresh coke to the generator, and for removing the clinker produced from the ash of the coke. The periods adopted for the length of the blow and run vary somewhat according to the nature of the coke and the available air pressure, a blow and run of 3 and 5 minutes and of 4 and 7 minutes being frequently adopted. The steam supply must be regulated so as not to allow a large excess of undecomposed steam to pass the fuel bed, as in that case a high percentage of carbon dioxide is formed. The checker work temperatures required vary with the class of oil used, the best results being obtained at somewhat different temperatures with different oils, as well as with the quantity of oil used per 1000 cub. ft. of gas made; an average temperature of working is about 750°.

The oil employed is mostly that fraction of petroleum lying between the burning oils and the lubricating oils, frequently termed 'solar' oil, which can be obtained at the lowest price. This is heated before introduction into the carburettor by passing through a coil in the gas main over which hot gas is passing. The amount of oil used depends upon the quality of gas which is desired, and is regulated according to the requirements in this respect.

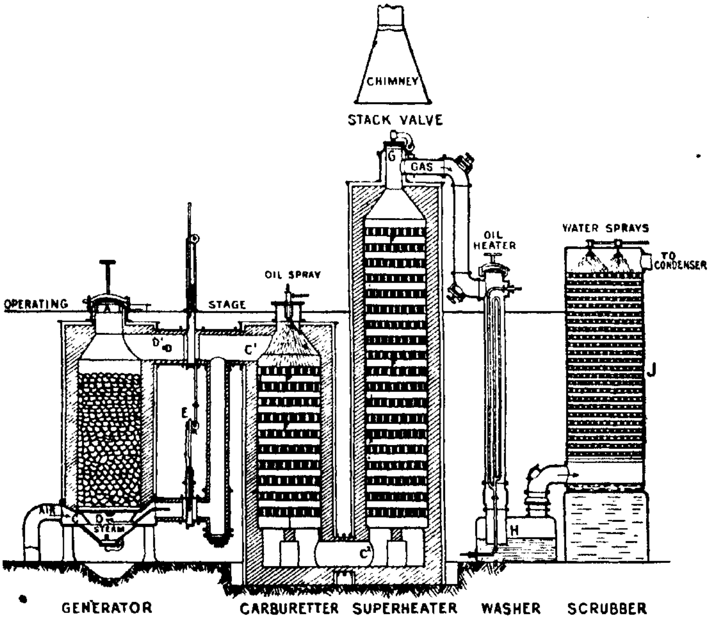


FIG. 25.

As the gas production is intermittent, a balancing reservoir is required for the gas if this is to be passed through the purifiers at a uniform rate. For this purpose a relief gas holder is placed at the condenser outlet into which the gas passes intermittently as made, and is drawn from it continuously by an exhauster and forced forward to the purifiers. The gas is purified from tar fog and sulphuretted hydrogen, and from carbon dioxide, if necessary, by the same methods as adopted with coal gas. Usually separate purifiers are employed for this gas, the purified streams of coal gas and carburetted water gas mixing together at the outlet of their respective meters before reaching the holders, but in some cases the crude carburetted water gas is mixed with the coal gas before the purifiers, and the mixed stream purified in the same boxes.

The only by-product obtained in the manufacture, other than spent oxide or spent lime from the purifiers, is the oil tar, no ammonia being produced in the process. The oil tar is a comparatively thin oil of sp.gr. 1·0–1·05, consisting mainly of aromatic hydrocarbons. It only contains about 30–35 p.c. of pitch, and scarcely any 'free carbon,' the solid matter found in it consisting chiefly of fine coke ash carried over from the generator with the stream of water gas. It is mostly sold to distillers, but is sometimes used as fuel, and also for washing the crude coal gas to remove naphthalene, or which it normally contains only small amounts. Sometimes the tar separates as an emulsion with water, from which the latter only separates with great difficulty.

The amount of coke employed in the manufacture, including that used for raising steam, amounts to from 40 to 50 lbs. per 1000 cub. ft. made, whilst the consumption of oil varies considerably, according to the quality of gas required. With good working each gallon of oil of good quality used per 1000 cub. ft. will give an illuminating power of 7–8 candles if the carbon dioxide is removed. The quantity of oil tar produced amounts to 12–15 p.c. of the oil used.

Carburetted water gas contains the same constituents as coal gas, but their relative amounts differ considerably, the percentages of carbon monoxide and ethylene being higher, and those of hydrogen and methane lower; it only contains small amounts of sulphur compounds other than sulphuretted hydrogen.

The following analyses of coal gas, carburetted water gas, and of a mixed gas containing about 20 p.c. of the latter, are fairly typical for gases of relatively high calorific power, and show the general character of the difference:—

	Coal gas	Carb. water gas	Mixed gas
Carbon dioxide . .	1·2	3·8	1·6
Ethylene and benzene	3·2	11·4	4·1
Oxygen . . .	0·4	0·2	0·5
Carbon monoxide .	9·1	31·0	12·2
Methane . . .	30·2	15·0	28·1
Hydrogen . . .	48·5	32·9	46·2
Nitrogen . . .	7·4	5·7	7·3

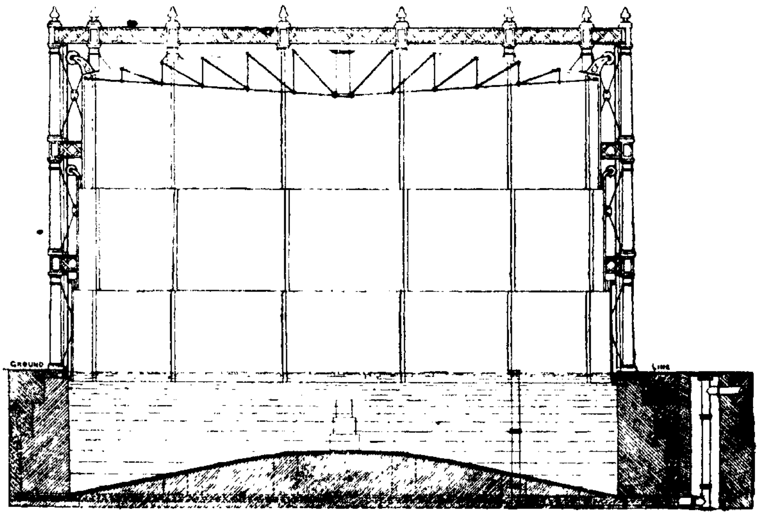
Carburetted water gas usually contains small amounts of ethane as well as methane.

The sp.gr. of carburetted water gas is much higher than that of coal gas of the same illuminating power, owing especially to its smaller percentage of hydrogen. It varies considerably, according to the percentage of oil gas in it, but usually falls within the limits of 0·6 and 0·75 (air=1).

Measurement, storage, and distribution of the gas. The gas, leaving the purifiers, passes to the station meters in which its volume is measured, and thence to the gas holders, where it is stored ready for distribution as required. The meters employed are usually wet meters, similar to those used as consumers' meters, but of very much larger size. The temperature of the gas passing and the height of the barometer is noted, and the volume recorded by the meter corrected to standard temperature and pressure, which is, however, not the 0° and 760 mm. barometer employed for scientific purposes, but that of the gas at 60°F. and 30 inches bar. saturated with moisture, this being approximately the average condition of the gas when sold to consumers, whose payment is made by volume.

The gas holders (Fig. 26), consisting of a large bell with suitable guide framing floating in a tank of water, are often of very large size, the largest being capable of holding about 15,000,000 cub. ft. In order to reduce the necessary depth of the tank, the bell is usually constructed in a number of lifts which slide into each other in a somewhat similar manner to the cylinders of a telescope. The weight of the holder keeps the gas within it under a pressure equivalent generally to the weight of a water column of 4–10 inches, according to the weight and diameter of the holder.

In order to control the pressure of the gas in



— SECTION THROUGH TANK AND GASHOLDER —

Fig. 26.

the mains in the district of supply, a governor is fixed between the holder and the trunk mains, whereby the pressure in the distribution mains is reduced to that most suitable, after which it is automatically maintained at that pressure. Fig. 27 gives a section of a governor in frequent use. The gas, entering in the direction shown by the arrows, must, in order to reach the outlet, pass through a device consisting of a hollow vertical cylinder closed at the top and having a number of slots cut in the vertical side, the width of which increases towards the top of the cylinder. The top of this cylinder is connected by a rod with the bell above, and is capable of moving freely up and down with this bell which is sealed in water. When water is allowed to run into the annular chamber in the bell, the latter increases in weight, and with the attached cylindrical device sinks, increasing the size of the openings through which the gas can pass, and by adjustment of the amount of water the desired pressure at the outlet can be obtained. If, then, owing to increased consumption, the pressure of the gas in the outlet main falls, this lessened pressure is transmitted to the bell, which, under the atmospheric pressure, falls, increasing the size of the gas openings, allowing more gas to pass and restoring the pressure in the outlet main. If the consumption decreases and pressure increases, the bell rises and reduces the size of the gas openings, and in this manner the pressure once set remains constant. When it is desired to alter the pressure in the outlet main to allow for the periods of higher or lower consumption on the district, water is either added to or run off from the annular chamber in the bell.

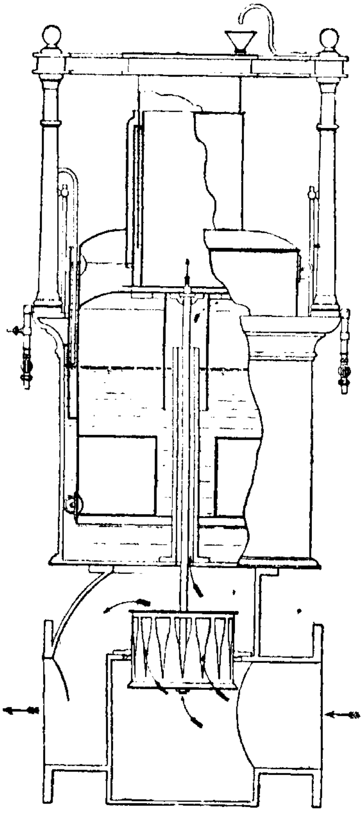


FIG. 27.

Formerly the holders gave more pressure than was required on the district, but at the present time, owing to the greater consumption and the higher pressures which are required for the efficient working of incandescent burners, gas fires, and gas engines, it frequently happens, especially in large works, that the pressure given by the smaller holders and the upper lifts of the larger ones is insufficient. In such cases the gas is drawn from the holder by means of fans, and forced forward at higher pressure to the works governor, or carried into the district by separate high-pressure mains, the gas from which is passed into the ordinary distribution mains at suitable points for maintaining good and uniform pressure throughout the area of supply.

Determination of calorific power. Several calorimeters are in use for this purpose, all of which are in principle identical with the form proposed by Hartley (J. Gas Lighting, 1884, 1142), the gas being burned at a constant rate in a chamber through which water also flows at a constant rate. The instrument in most frequent use in all parts of the world is the Junkers' calorimeter, a section of which is given in Fig. 28. The gas, after passing through a governor and meter, is burned in a large Bunsen burner, E, in the central portion of an annular copper chamber, the annular space of which is traversed by a large number of copper tubes down which the products of combustion pass and escape into the atmosphere by the side opening F, which is provided with a damper regulating the amount of air passing through the apparatus. The water of a temperature closely approximating to that of the normal is run into the upper small reservoir A, provided with an outlet proper to the calorimeter, and a constant level overflow B, the rate at which the water enters being maintained above that passing through the calorimeter, the excess passing away by the overflow, thus maintaining a constant head of water. The water flows down, past the regulating cock and inlet thermometer, to the bottom of the annular chamber, and flows upwards to the top around the tubes conveying the products of combustion in the reverse direction, and cools the latter to the temperature of the incoming water. The water leaves the annular chamber at the top and passes through a series of baffle plates to ensure thorough mixing, over the outlet thermometer to the overflow funnel C. The water condensed from the gas collects at the bottom of the annular chamber and flows out through a small tube into a collecting cylinder.

The gas and water supplies are adjusted so that the difference in the readings of the inlet and outlet water thermometers is 10°–15°, and when equilibrium is attained and the condensed water is also dripping regularly from the small tube, D, at the bottom of the calorimeter, the water from the calorimeter is diverted into a collecting vessel as the meter hand passes a point which is noted, and a small measuring cylinder placed to collect the condensed water. Frequent readings of the inlet and outlet thermometers are made, until a sufficient amount of water has been collected (from 2 to 5 litres are mostly taken); to conclude the test, the gas may be shut off when the collecting vessel is filled to a definite point, or the water may be diverted from the measuring vessel as the meter hand passes a noted point. The volume of gas is taken from the meter readings and corrected to that of the moist gas at 60°F. and 30 inches bar., the weight of water passed determined by measurement or by weighing, and the average increase in temperature of the water found from the readings taken during the test. The calorific power of 1 cub. ft. of the gas, expressed in large calories, is equal to:

$$\frac{\text{weight of water in kilos.} \times \text{temperature C.}^\circ}{\text{volume of gas consumed}}$$

In this country the value is usually expressed in British thermal units, *i.e.* the amount of heat required to raise 1 lb. of water 1°F., each calorie being equal to 3·968 B.Th.U., and to obtain the result in these units the number of calories found must be multiplied by that factor.

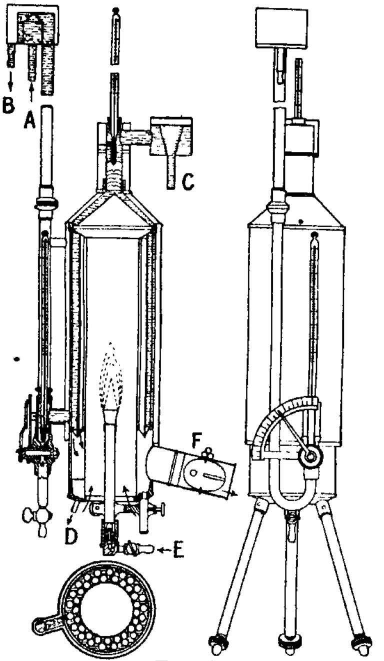


Fig. 28.

The calorific value thus obtained includes the latent heat evolved by the condensation of the steam produced by the combustion of the hydrogen contained in the gas, and is termed the *gross* calorific power. In almost all the practical applications of gas, the products of combustion pass away at temperature above which the condensation of the steam occurs, so that this latent heat cannot be utilised either for the production of high temperature in the flame of the burning gas, or for development of power in the cylinder of a gas engine. A deduction of this amount of latent heat is therefore made from the gross calorific power, the difference, excluding this heat, being termed the *net* calorific power. The amount of such latent heat is ascertained by collecting the condensed water which flows from the calorimeter during the test, a larger volume of gas than that required for the determination of the gross value being burned for this determination (about 1 cub. ft.). Each c.c. of water evolves, in condensation, 0·536 cal., and the amount to be deducted is found by multiplying 0·536 by the number of c.c. of condensed water per cub. foot of gas burned. The usual practice is, however, to deduct 0·6 cal. for each c.c. of condensed water, this representing not only the latent heat, but also the sensible heat lost by the condensed steam in cooling from 100° to atmospheric temperature, and the 'net' figures then obtained are rather lower than the true net value, which has to be employed in thermodynamic calculations.

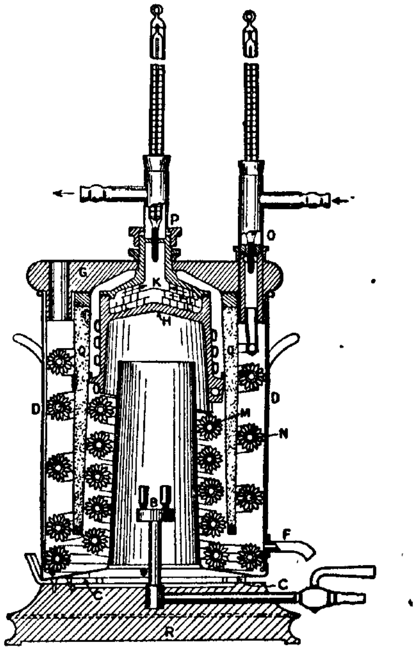


Fig. 29.

The Boys calorimeter, prescribed by the Metropolitan Gas Referees, is shown in section in Fig. 29. The base R carries the pair of union jet burners B, which are supplied with the gas to be tested through a governor and meter; the calorimeter vessel proper D, after lighting the gas, is then placed in position over the flame, and rests on three centering and lifting plates C, leaving a space through which the air required for combustion enters. The products pass up the copper chimney and thence into the annular space between the chimney and the outer side of the calorimeter vessel. This annular space is divided into two portions by a brattice of thin sheet brass filled with non-conducting material such as cork-dust, which causes the combustion products to pass first down the inner portion of the annular space, and then up on the outer side to the top, where they escape into the atmosphere through holes bored in the wooden top. A tube of copper, to the outside of which is sweated a helix of copper wire, giving it a large conducting surface, is led in a spiral, first from top to bottom of the outer annular chamber, then around the bottom below the brattice, and finally up the inner annular chamber. The water is led over the inlet thermometer through this tube, passing first through the outer annular chamber, then along the bottom, into which water is placed before commencing a test, and up the inner annular chamber, and in its travel absorbs the heat of the products of combustion. Before reaching the outlet thermometer, the water passes through the central temperature-equalising chamber.

The general method of working is similar to that of the Junkers calorimeter, full details of construction and working being given in the official notification of the Gas Referees (Wyman and Sons, Ltd.).

With both these forms of calorimeter, an appreciable error is introduced into the determination of the gross value, if the air supply to the calorimeter is not at least 90 p.c saturated with moisture, inasmuch as the waste gases, which always leave the calorimeter in a saturated condition, then carry away with them a portion of the steam formed by the combustion of the gas without its undergoing condensation, and the latent heat of this portion of the steam is therefore not included. A correction should therefore be made on this account (Met. Gas Referees Notification).

The Simmance-Abady 'total-heat' calorimeter, made by A. Wright and Co., Ltd., is a modification of the original Hartley calorimeter made by the same firm, and in general method of working closely resembles the Junkers' calorimeter. It differs from it especially in that the water overflow from the upper constant level chamber of the apparatus acts as an injector, and forces through the calorimeter the necessary volume of air for the combustion of the gas. In this manner it is automatically ensured that water, air, and waste gases are all at very nearly the same temperature, and also that the air passing through the calorimeter is saturated with moisture, thus obviating any necessity for correction in the latter respect.

Recording calorimeters, such as those of Beazley and Simmance-Abady, giving a continous record of the calorific power of gas, are also largely in use. (For details of the necessary precautions to obtain accurate results in gas calorimetry, *see* J. Gas Lighting, 1908, 104, 904; Coste, J. Soc. Chem. Ind. 1909, 28, 1231.)

Illuminating power. The statutory methods of determination of the illuminating power of coal gas, when burned in open flames, have been described fully in former editions, but in view of the abandonment of this test for statutory purposes, and its replacement by a calorific power test, and the small importance now attaching to such tests in practice, the description is omitted here; for information on the matter reference may be made to former editions or to the Official Notification of the Metropolitan Gas Referees for the years 1910–1918.

Photometric observations are, however, still required in connection with coal gas where it is used for illumination, such as in the determination of the illuminating power of incandescent burners, the amount of light emitted by the different burners at varying angles, and the actual illumination of indoor and outdoor surfaces. Space will not allow of the consideration here of the necessarily somewhat complicated apparatus required for these applications.

Whilst the most important property of gas is its calorific power, which is, in fact, its total potential energy, expressed in heat units, it must be remembered that this is not the only factor to be considered. The efficiency of the apparatus in which the gas is used depends, in a large number of cases, not only on the total amount of heat liberated, but also on the temperature and other properties of the flame produced. The presence of large quantities of inert incombustible gases, such as nitrogen and carbon dioxide, lowers the flame temperature at a greater rate than it does the calorific power, and although their presence in coal gas cannot be altogether avoided, it is desirable that their amount should be kept as low as possible consistently with economical working in other respects. Further, the average flame temperature in burners of the Bunsen type, by which most of the gas made is now consumed, varies greatly according to the volume of primary air drawn into the gas before combustion by the injecting action of the gas jet issuing from the burner nozzle, as the most suitable proportion depends upon the composition of the gas, and the actual amount of air drawn in varies according to both the pressure and the sp.gr. of the gas; if, therefore, an apparatus is set to give the greatest efficiency under certain conditions of pressure, composition, and sp.gr. of the gas, this efficiency will not be maintained if the gas supply undergoes considerable variations in any or all of these points. Further, the efficiency of many kinds of gas apparatus—for example, the incandescent mantle, and the columnar radiants of gas fires—depends, to a very large extent, on the exact fitting of these into the hottest part of the flame, and variations of the above conditions tend to alter the shape of the flame and often thereby very materially reduce the efficiency of the apparatus.

Whilst there is very considerable difference of opinion both within and without the gas industry with regard to the most suitable calorific power for a public supply under present conditions, having regard to the greatly varying purposes for which it is now employed, there is general agreement that, whatever the actual calorific power fixed on may be, both this and the volume of air required for combustion of unit volume of gas, its pressure and its sp.gr. should be then maintained as regular as possible, and that, from the consumer's point of view, better results ensue from a supply of fairly uniform, although lower average, calorific power, with reasonable constancy of pressure, air requirement, and sp.gr., than with gas of considerably higher calorific power, but subject to much greater fluctuations in these respects. Whilst it is not practicable to obtain exact uniformity of calorific power, composition, and sp.gr., or of pressure throughout a large district of supply, except at a cost which would be prohibitive, it is of the greatest importance for all concerned that this end should be aimed at so far as it can be effected with reasonable economy.

Sulphuretted hydrogen. All gas supplied for public use must by law be free from sulphuretted hydrogen. According to the stipulations of the Gas Works Clauses Act, the gas, when passed for 3 minutes over bibulous paper moistened with lead acetate solution at the rate of 5 cub. ft. per hour, shall not darken the paper, owing to the formation of lead sulphide. As the formation of a brown stain in this manner is an exceedingly delicate test for sulphuretted hydrogen, this means that for all practical purposes the gas passing the test is free from that impurity.

Determination of total sulphur. The official method for estimation of the total sulphur present in purified gas is that prescribed by the Metropolitan Gas Referees, which is illustrated in Fig. 30. The gas, if it is also to be tested for sulphuretted hydrogen and ammonia, is passed first over test papers made by soaking blotting paper in a 10 p.c. solution of lead acetate, and exposing such slips, whilst damp, to an atmosphere containing ammonia, and then over a cylinder filled with glass beads or broken glass, moistened with a known volume of standard sulphuric acid, to remove ammonia. It is then burned in a small Bunsen burner at the rate of 0·5–0·7 cub. ft. per hour until 10 cub. ft. have passed, the flame being surrounded by lumps of commercial ammonium carbonate. The products of combustion, together with ammonia, pass by means of the trumpet tube into the glass cylinders provided with a tubulus at the bottom for connecting with the trumpet tube; the upper portion of the cylinder is filled up with glass marbles, and from the top a wide bent-glass tube is led, which acts as a chimney and final condenser. A small tube drawn out to a jet conveys the condensed products to a flask or beaker placed on a shelf below. The sulphur dioxide formed by the combustion of the sulphur condenses in presence of the moisture, excess of oxygen and ammonia forming a solution of ammonium sulphate, and when the required amount of gas has been burned, the cylinder is washed out with water, and the sulphur present in the liquor estimated as barium sulphate in the usual manner, the amount being calculated as grains of sulphur per 100 feet. This method tends to give slightly low results, as the sulphurous acid primarily formed is not always completely oxidised to sulphuric acid, and escapes precipitation with barium chloride, on which account many prefer a previous treatment of the solution with bromine, or precipitation with nitric acid and barium nitrate. The sulphur estimation may also be made by aspirating the products of combustion through wash bottles containing sodium hypobromite solution, and subsequent precipitation of barium sulphate, or through neutral hydrogen peroxide, the sulphuric acid produced in the latter case being determined by titration with standard alkali.

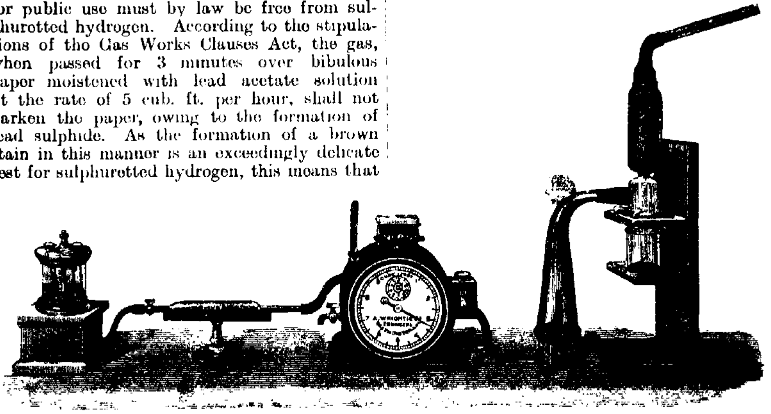


Fig. 30.

Employment of coal gas. At the present time, coal gas is employed for a very great and increasing diversity of purposes. Whereas during the first 60–70 years of the existence of the industry its employment was almost entirely employed for illumination by burning it in open-flame burners of various kinds, the proportion of the gas now burned in this manner has become very small. Where gas is employed for illumination now, as is still largely the case, the light is obtained by the much more efficient incandescent burner.

In these last, the development of light is obtained by raising to incandescence a mantle composed essentially of thoria, to which about 1 p.c. of ceria has been added. The manufacture of these mantles is dealt with in a separate article (*see* Gas mantles). In order to raise such mantles to incandescence, the gas is burned in a non-luminous flame of the Bunsen type, by mixing with the gas a certain proportion of primary air before it undergoes combustion, when it burns with the well-known non-luminous flame, having a definite two-coned structure.

Whilst the actual causes of the high development of light from such a mantle are still a matter of dispute, there is no question that the amount of light emitted increases greatly with the temperature to which the mantle is raised. In order, therefore, to obtain the highest practical efficiency with such burners, the gas must be burned in such a manner as to produce a flame of high temperature, and this must also have such a shape that the mantle is situated in the zone of highest temperature.

The effect of the introduction of the primary air to the gas before combustion is that in the flame the gas first undergoes combustion with the limited amount of oxygen present in it, yielding a mixture of steam, carbon dioxide, hydrogen, and carbon monoxide, together with the nitrogen of the added air, this reaction taking place in the area visible as the 'inner cone,' all hydrocarbons completely disappearing from the gas, provided the amount of oxygen in the mixed gas undergoing combustion is rather more than half that required for its complete oxidation. This mixture of 'water gas' and nitrogen forms the 'outer cone' of the flame, which has itself been raised to a very high temperature by the reactions occurring in the inner cone, and the hydrogen and carbon monoxide then burn where the air is in contact with the outer cone, further increasing the temperature at this surface, and the relative shape of flame and mantle should be so arranged that the latter occupies as nearly as possible the zone in which this final oxidation is taking place.

The higher the proportion of primary air added, the smaller is the size of the flame, and especially of the inner cone, and the higher the average temperature of the flame, the highest efficiency of an incandescent burner being obtained when the amount of primary air added is equal to that theoretically required for the complete combustion of the gas. Under ordinary conditions of gas supply, however, this condition cannot be obtained, as a mixture of gas with the full amount of air is highly explosive and the explosion wave travels back from the flame at a velocity greater than that of the advancing mixture of gases, and the burner 'fires back,' the gas then igniting at the injector nozzle. Under ordinary conditions, it is not practicable to admit as primary air more than about two-fifths to four-fifths of the total amount required for complete combustion. On the other hand, if the proportion of primary air admitted is too low, the hydrocarbons of the gas are not completely converted into water gas in the inner cone, some hydrocarbons passing to the outer cone, in which case, apart from the lower temperature of the flame produced, carbon may be deposited on the mantle, which becomes blackened, and its light emission thereby greatly reduced.

The proportion of primary air drawn in through the air holes of the burner depends, not only on the construction of the latter, but also to a very large extent on the pressure of the gas and its specific gravity. The higher the pressure of the gas, and the lower its specific gravity, the smaller is the opening which is necessary for the passage of the required amount of gas, and the higher its velocity, and it is largely the latter factor which determines the amount of air sucked in through the air holes. On this account the pressure at which the gas must now be supplied is much higher than was necessary for flat-flame burners, and should be equal to that of a water column at least 2 inches in height; with lower pressures, especially with higher qualities of gas, it is much more difficult to get a well-aërated flame, and to avoid the deposition of carbon on the mantles.

With the upright incandescent burners, first introduced and still largely in use, the flame burns from the top of the burner. The central portion of the burner head is solid, so that the flame produced is annular, the central closed portion having a socket in which is placed the fire-clay crutch supporting the mantle, and the annular space covered with wire gauze or similar device to prevent 'flashing back.' To obtain a good efficiency, the size of the gas nozzle and air holes of the burner must be adjusted so that, under the average pressure existing at the burner, a well-aërated flame is produced, having only a small inner cone, and of such a size that the mantle, when put on, lies fully in the zone of highest temperature. When adjusted to give the best results, an efficiency of 25–30 candles per cub. ft. of gas having a calorific power of 530 B.Th.U. can be obtained, although, as the mantle ages, this tends to fall off, largely owing to alterations in shape of the mantle, which cause portions of it to occupy positions of lower temperature in the flame. Periodic cleaning of the burner is also necessary, as the dust in the air drawn in tends to settle on the gas nozzle and on the wire gauze of the burner head, and results in less air being drawn in and the production of an under-aërated flame of lower temperature.

In the inverted incandescent burner, which is now largely replacing the upright burner, the flame is directed downwards, the mouth of the burner being in this case fully open, and the mantle supported from above on a ring of fire-resisting material attached to the burner, this form possessing the great advantage that no shadows are thrown on the surfaces below, which are in most cases those which it is specially desired to illuminate. The proper adjustment of gas and air supplies, and a sufficient gas pressure, as well as the periodic cleaning of the burners from dust, is equally necessary with the inverted form, but when working under the most favourable conditions, these are more efficient than the upright burners, over 40 candles per cub. ft. of 540 B.Th.U. gas at moderate pressures.

By considerably increasing the pressure at which the gas is supplied, namely, to one equal to a column of about 55 inches of water or higher, much higher efficiencies are obtained, both with the upright and with the inverted burners. With the increased pressure, the velocity at which the gas can be made to issue from the injector nozzle is so increased, that the full amount of air necessary for its combustion can be drawn in through the air holes, and the mixture forced with much higher velocity through the burner, so that the tendency of the flame to flash back through the highly explosive mixture can be controlled, and a flame of very high temperature produced, resulting in a much greater light emission from the mantle on which the flame acts. With such high-pressure burners, efficiencies of as high as 70 candles per cub. ft. are obtained. High-pressure installations are now very largely adopted for outside lighting of the public streets and yards, and also for interior lighting in workshops and large public buildings, special plant being usually erected for compressing the gas for each installation, or in some large towns a special high-pressure main is laid from the works or some central point for the supply of gas under such higher pressure where it is required.

Although very large quantities of coal gas are consumed for illumination purposes in incandescent burners, a still larger proportion of the gas output is now employed for other purposes, the most important uses being for heating with gas fires, cooking by gas, and for power production in gas-engines. In industrial districts especially steadily increasing quantities are employed for very diverse purposes, including gas furnaces for metal melting, annealing, gas-fired kilns, &c. For many of these purposes, as with the incandescent burner, better efficiency can frequently be obtained by the use of gas under much higher pressure than that at which it is normally supplied, and suitable compressing plant is frequently installed at individual works for this purpose, or, in some cases where high-pressure gas is required by a large number of consumers in a limited area, special high-pressure mains are laid in that district by the gas undertaking, who then carry out the compression. Previous to the outbreak of the war, rapid increase in the amount used for all purposes was taking place, especially in industrial districts, and although the abnormal conditions since then have lessened the requirements in many cases, in other districts largely engaged on war industries, the demand increased to an extent which could not be fully met at the time. It is confidently anticipated that when new post-war 'normal' conditions are reached, and it is possible to provide increased manufacturing and distribution plant, a further large development in the employment of gas for these and for fresh purposes will take place. H. G. C.

GAS, DOWSON, *v.* GAS, WATER.

GAS, GENERATOR, *v.* GAS, WATER.

GAS MANTLES. The discovery, by Goldsworthy Gurney, in 1826, that a piece of dense lime held in the oxy-hydrogen blowpipe flame, gave rise to intense incandescence, may be taken as the starting-point of the uilitsation of this phenomenon for the generation of light, as Gurney's discovery was soon afterwards employed in practice by Drummond, who utilised the light whilst making a survey of Ireland; hence it was often known by his name, but is now more frequently called the oxy-hydrogen or lime-light.

The amount of heat necessary to raise a substance to the temperature needed for incandescence depends largely upon the size of the mass to be heated, as the larger it is the more will radiation and conduction tend to prevent the temperature of incandescence being attained, and when, soon after the discovery of the lime light, it was attempted to utilise incandescence for public lighting in Paris, the lime cylinder was replaced by small buttons of zirconia and magnesia, which, being more resistant to atmospheric influences than the lime cylinders, and being far smaller, lasted for a longer period and could more easily be raised to the required temperature

In this experiment, oxy-coal-gas burners were employed as the heating medium, but the expense soon led to its abandonment. In 1835 Talbot noticed that when a piece of blotting paper was dipped in a solution of a lime salt and was then incinerated in a spirit lamp, the ash which was left, consisting chiefly of lime, was so finely divided that the heat of a spirit-lamp flame was sufficient to raise it to high incandescence.

These early experiments pointed merely to the fact that if a refractory material like lime could be obtained in a sufficiently coherent and finely divided condition, a moderately hot flame would raise it to a temperature at which it would become usefully incandescent.

In 1848 Gillard, in attempting to utilise water gas for lighting as well as heating purposes, made a mantle of fine platinum wire, which, heated to incandescence in the flame, answered its purpose and emitted light for a short period, whilst in 1883 the Fahnehjelm comb (Fig. 1) was introduced for developing light from a flat water-gas flame. It consisted of fine rods of magnesia in a metal setting, which was fixed at the requisite height above a flat-flame burner consuming water gas, and from it a light of about 4½ candles per cub. ft. of gas consumed could be obtained.

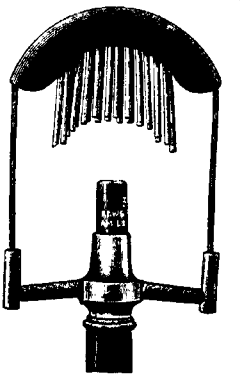


FIG. 1.

Up to the middle of last century, the flame of water gas or of alcohol vapour were the only ones that could have been used to incandesce finely divided refractory material, owing to the deposition of carbon from any luminous flame, but the introduction by Bunsen of the atmospheric burner in the early fifties rendered coal gas available for all heating purposes, and made the mantle a practical possibility.

About 1883 Clamond introduced a form of

mantle, consisting of a conical basket of threads of calcined magnesia, which was supported with its apex downwards in a small platinum cage, a flame of coal gas and air being driven down upon it under pressure. It was not, however, until a year later that Dr. Auer von Welsbach, working in Bunsen's laboratory at Heidelberg upon the rare earths, noticed that the oxides of some of the rare metals had a wonderful power of light emissivity when incandescent, and, following up this clue, made the brilliant series of discoveries which gave the world the incandescent mantle.

These discoveries took place in three distinct stages. In his work prior to 1885 he discovered the fact that if a cotton fabric be saturated with a solution of the nitrates of the rare earths, and be then carefully incinerated, an ash is left which is an exact simulacrum of the original fabric, although the burning out of the cellulose reduces it to about one-third of its former size, so that by making a cotton sleeve about three times the size of the Bunsen flame it was intended to fit, saturating it in a solution of the nitrates of the metals of which he required the oxides, and then carefully burning it off over a blowpipe flame, he could obtain a mantle which would fit the outer zone of the Bunsen flame, and, being there heated to incandescence, would emit a useful amount of light.

His first patent, taken out in 1885, covered this part of his invention, and specifies the mixtures of oxides, which he gives as :

60 p.c. of zirconia, or oxide of zirconium.
20 p.c. of oxide of lanthanum.
20 p.c. of oxide of yttrium.

This last oxide may be omitted, and the proportions may be :

50 p.c of oxide of zirconium.
50 p.c. of oxide of lanthanum.

In place of the oxide of yttrium, ytterite earth may be used, whilst cerite earth containing no didymium and but little cerium may be employed to replace the oxide of lanthanum.

These first mantles were a commercial failure, as they gave a light very little in excess of that yielded by the Clamond basket, and they were so fragile in character that they were unable to withstand the slightest shock.

The amount of light yielded by these mantles varied from 3 to 6 candles per cub. ft. of gas consumed, but it was exceptional to meet with the higher value. Using the purer materials now obtainable, however, mantles made according to the formulæ of the 1885 patent give the following results :—

Composition of mantle	P.c.	Gas consumed cub. ft.	Illuminating power. Total candles	Illuminating power. Candles per cub. ft.
I.				
Zirconia	60	5·4	12·9	2·4
Lanthana	20			
Yttria	20			
II.				
Zirconia	50	5·5	9·4	1·7
Lanthana	50			

The lower candle power obtained with mantles made of the purer salts points to the fact that the impurities of the compounds at first employed endowed the older mantles with much of the illuminating power, so that no uniformity in results could be expected, besides which the mixtures of oxides used were continually being varied in hopes of obtaining better results.

In 1886 the second Welsbach patent appeared. This covered the use of thoria either *per se* or mixed with oxides of other rare metals, and it is clear that at this period Welsbach imagined that the oxide of thorium alone had a very high power of light emissivity, but, as a fact, a mantle made of pure thoria emits practically no light, and the amount of light obtainable was due to traces of ceria, which had not been eliminated from the thorium salt in its preparation from thorite and orangite.

Later on, Welsbach discovered this fact, and also found that the addition to thoria of traces of ceria endowed it with the wonderful power of emitting light possessed by the modern mantle, and Mr. Moeller, of the Welsbach Company, took out a patent in England in 1893, in which he protected the use of thoria in combination with very small traces, not exceeding 1 or 2 p.c., of oxides of other rare metals, amongst which was cerium. It was only at this date that the incandescent mantle began to be a commercial success, and in spite of the thousands of experiments which have since been made, no mixture of oxides has been discovered which will give a light comparable with that yielded by the mixture of 99 p.c. thoria with 1 p.c. ceria, which is now universally used in mantle manufacture.

The oxides which can be used in making an incandescent mantle are limited in number, owing to the fact that they must be able to resist atmospheric influences, must be sufficiently refractory to withstand the temperature of the flame for a very long period, and must not be liable to excessive shrinkage during the burning off of the cotton fabric.

The oxides in the following table are those which most nearly fulfil such requirements, and the light given by mantles made from the commercial as well as from the carefully purified salts shows the vast differences that traces of impurity make in their power of emitting light :—

Light emitted per Cubic Foot of Gas by Various Oxides.

		Pure	Commercial
Metallic oxides :			
Zirconia		1·5	3·1
Thoria		0·5	6·0
Earth metals :			
Cerite earths	Ceria	0·4	0·9
	Lanthana	—	6·0
Ytterite earths	Yttria	—	3·2
	Erbia	0·6	1·7
Common earths	Chromium oxide	0·4	0·4
	Alumina	0·6	0·6
Alkaline earth metals :			
Baryta		3·3	3·3
Strontia		5·2	5·5
Magnesia		5·0	5·0

If these oxides be examined for shrinkage, duration, and strength, it is found that only three of them, zirconia, alumina, and thoria, are suitable as the basis of the mantle, and even with these three, zirconia in the hottest part of the flame is liable to considerable and rapid shrinkage, whilst with alumina there is also slow volatilisation, so that the life of the mantle is gradually shortened by the slow wasting away of the threads of the mantle structure. The nitrate of thorium, unlike those of the other earths, has the property of adsorbing from 1 to 1·2 p.c. of thorium sulphate, and when a fabric of vegetable fibre saturated with a solution of thorium nitrate containing from 1·5 to 2 p.c. of sulphate is burned, the decomposition, towards the end of the operation, of this sulphate results in a minimum of shrinkage and gives to the oxide skeleton a spongy character, which permits of its being readily shaped and its finer particles rapidly fritted by a high-temperature blowpipe flame, leaving a mantle of regular form, comparative rigidity, and very large radiating surface. The oxide is refractory under the heat of an atmospheric burner for a much longer time than any other known.

The porous mass resulting from the incineration of the nitrate containing a small proportion of sulphate occupies more than ten times the volume of the original nitrate. This means that the resulting mass is of a spongy character, containing an enormous number of little air cells, which must render it an excellent non-conductor of heat. A mantle made of pure thoria gives practically no light, but if successive small additions of ceria be made to it, the light emitted gradually increases until a ratio of 99 p.c. thoria to 1 of ceria is reached, when the maximum illuminating effect is obtained. The light diminishes with further additions of ceria till, with 10 p.c. of ceria in the mixture, the mantle once more gives practically no illumination. No expansion takes place during the conversion of the cerium nitrate into oxide, the latter occupying about the same amount of space as the original nitrate, hence in the mantle, although the ratio of thoria to ceria is as 99 to 1 by weight, yet by volume it is as 999 to 1.

In the commercial manufacture of mantles, a cotton fabric was first employed knitted in the form of hose, the diameter of which was controlled by the number of needles on the knitting machine, which varied from 70 to 90, the size generally used being knitted by a 85-needle machine, giving to the finished fabric a diameter of 2¼ inches. The resultant hose is cut into suitable lengths, and one end turned over and sewn with thread to form the head of the mantle (which after impregnation and drying is drawn together with asbestos thread to form the top and a loop for suspension). These lengths are then saturated with the impregnating solution. This consists of a solution (approximately 30–35 p.c. by weight of solids) of the nitrate of thorium with 1 p.c. of cerium in water, there being added thorium sulphate, and from 0·7 to 1·5 p.c. of nitrates of other metals, *e.g.* magnesium, aluminium, calcium, glucinum, zirconium, yttrium, whose function is either to increase the porosity of or facilitate the fritting of the skeleton. One suitable formula is 1 kg. thorium nitrate, 10 grams cerium nitrate, 2 grams magnesium, 1 gram calcium, 7 grams glucinum nitrates, in 2 kilos of water. The mantles then pass through rollers, which are under pressure in order to squeeze out the excess of solution, leaving the fabric retaining the quantity that will give a satisfactory skeleton of oxides after incineration, and this quantity may be taken as 0·7 gram on the rough or 0·5 gram on the finished mantle after trimming. The soaked lengths are next stretched upon glass or papier mâché forms in a drying chamber, the temperature of which is maintained between 80° and 90°F. (27° to 32°C.). The head of the mantle is treated with a solution of magnesium, aluminium, and other nitrates, the object being to strengthen this part, which is the most liable to breakage. They are again dried, sewn with asbestos thread and 'moulded' by stretching on a wooden mould in order to give them the necessary shape for the next operation, that of 'burning off.' This is done upon suitable blowpipe burners supplied with gas or air under pressure, which gives a flame of a very high temperature, and these are mounted in such a way that either the burner or the mantle can be raised or lowered at the will of the operator, so that the flame can be made to play on every part, until the whole of the mantle has been shaped and hardened, leaving a skeleton of oxides formed by the decomposition of the nitrates of the salts employed. This skeleton is carefully dipped in a solution of collodion, an average formula for this solution being :

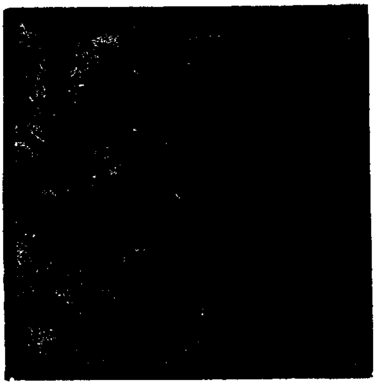


FIG. 2.—COTTON MANTLE BEFORE BURNING OFF.

4 p.c. collodion	. 20·0	parts
Ether . .	. 18·3	,,
Castor oil .	. 0·96	,,
Camphor .	. 1·5	,,

the two latter ingredients being added to prevent over-contraction on drying. After dipping, the mantles are dried in steam-heated air or vacuum ovens to allow the solvents to evaporate, and they are then trimmed and packed.

As soon as the incandescent mantle became a success, many attempts were made to evade the Welsbach patents, and the most successful of these consisted in impregnating a solution of nitrocellulose in ether and alcohol with the nitrates of thorium and cerium, and squirting the mixture out through minute orifices in the same way that artificial collodion silk is made. These filaments were then woven into mantle hose, and the collodion basis was denitrated by soaking in an alkaline sulphide, and after [illegible] and drying, the mantle was made from it by the same process as with impregnated cotton. It was found that mantles made in this way were distinctly superior to the cotton mantles, both in life and light emissivity, this being due to the difference of the structure of the thoria-ceria residue, which is shown in the photomicrographs, from which it is seen that the cotton (Figs. 2 to 5) gives a closely twisted rope of minute fibres, whilst the collodion (Figs. 6 and 7) gives a bundle of separate filaments without excessive twist or plait.

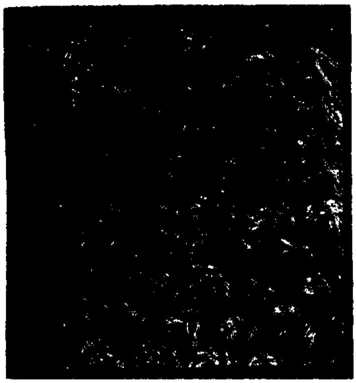


Fig. 3.—After burning off.

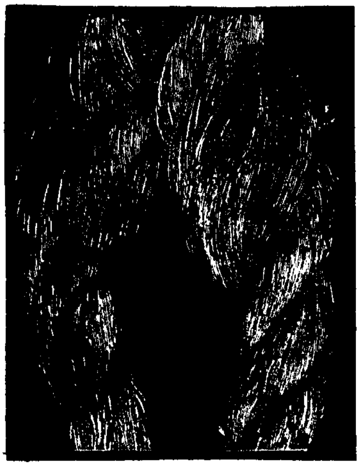


Fig. 4.—Cotton before burning off.

The advantages of the collodion mantle were, however, discounted by the cost, which was much higher than that of the cotton fabric, and attempts were made to find a substitute for cotton which would give the same results as the collodion at a cheaper price, and this was found in ramie fibre, which has now almost entirely replaced cotton for mantle manufacture.

The ramie fibre is produced from a plant of the nettle class, *Boehmeria tenacissima*, and when freed from its glutinous coating can be woven into a beautiful silk-like material, and when the ramie thread is knitted, impregnated, and made into mantles, the structure is seen to far more nearly approach that of the collodion than of the cotton fabric (Figs. 8 and 9).

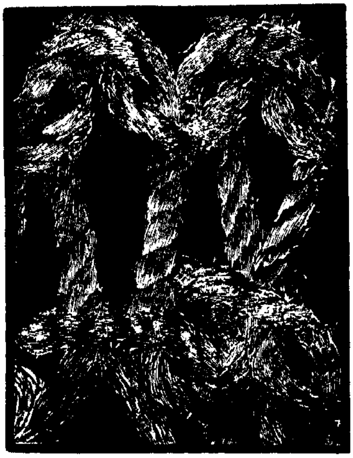


Fig. 5.—Cotton after burning off.

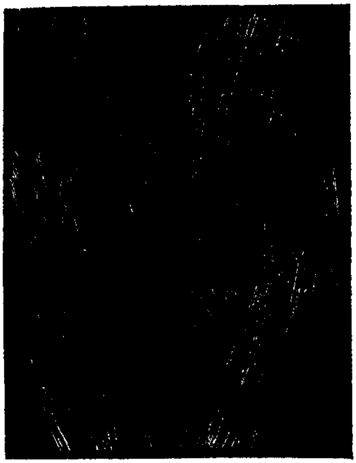


Fig. 6.—Collodion before burning off.

A mantle with a basis of collodion fibre is again coming into favour, particularly in connection with lighting by high-pressure gas. Artificial silk made by the Viscose process is impregnated in a nitrate solution, the nitrate converted into hydrate by treatment with ammonia, ammonium sulphide, hydrogen peroxide, &c., and the fabric incinerated in the ordinary way.

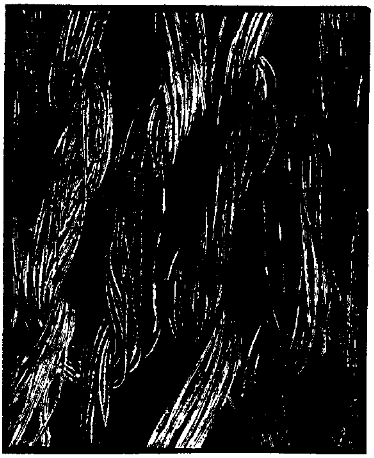


FIG. 7.—COLLODION AFTER BURNING OFF.

Threads of this material are thin, strong, and capable of heavier impregnation than either cotton or ramie threads. Artificial fibre also possesses the advantage of uniformity of composition, diameter, and other physical properties, and gives a mantle which is more durable, is a more constant light producer, and does not undergo shrinkage.

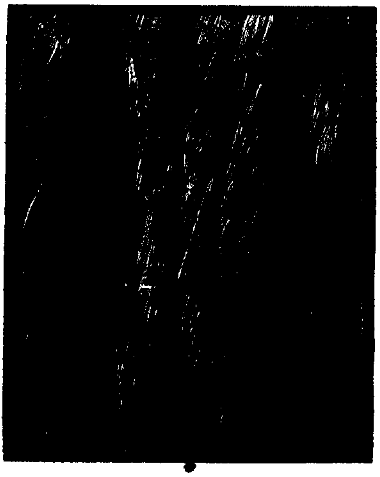


FIG. 8.—RAMIE BEFORE BURNING OFF.

Up to 1900, all the mantles used were of the upright type, supported in the atmospheric burner flame by a central rod of magnesia or an outside iron support from which the mantle was suspended, but owing to the slightly conical shape of the mantle, the maximum light was thrown at an angle a few degrees above the horizontal, whilst the shadow of the fitting was thrown on the surfaces immediately below the burner. In order to overcome this trouble, the idea was introduced by Kent, in 1897, of making an atmospheric burner with a long mixing tube, the end of which was turned downwards and the flame made to burn in an inverted mantle. It was not, however, until after 1900 that the introduction of the present forms of inverted burner and mantle popularised the idea, which has many advantages in districts where the gas is supplied at a pressure of not less than $\frac{20}{10}$ths, *i.e.* 2 inches of water pressure.

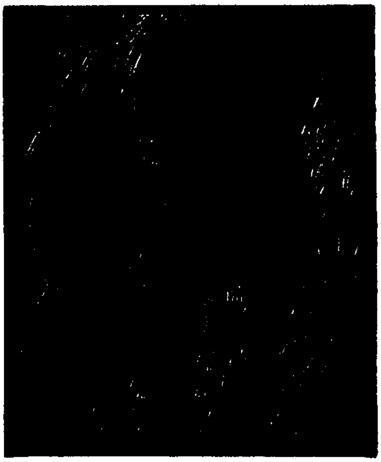


FIG. 9.—RAMIE AFTER BURNING OFF.

With the inverted mantle, the maximum light is thrown downwards at an angle of 45° below the horizontal, whilst there is no shadow, and the mantle, being fixed to a fire-clay ring which is suspended from lugs on the burner tube, is far less likely to be injured by vibration than is the case with the upright mantle, which needs an anti-vibrator on the burner if used for street lighting where there is heavy traffic, whilst the slight preheating of the gas and air supply, and the fact that the flame is not hurried away from the mantle as in the case of the upright burner, bring the duty of the mantle up to 25 to 30 candles per cub. ft. of gas consumed.

In making the inverted mantle, the same methods are employed as with the upright, except that the bottom of the fabric is sewn up, after impregnating, squeezing, and drying, with a thread of the same impregnated material, and the top of the hose is bound on to the fire-clay supporting ring with asbestos thread before burning off and shaping.

The burners used with the earliest upright incandescent mantles were small Bunsens of the ordinary type, with a tube about 4 inches in length, fitted with a gallery to carry a chimney and a head stamped out of thin sheet metal. This made a very long fitting which proved an objection in many cases where flat-flame or argand burners had been employed, the result being that the burner tube was shortened, and the head carrying the gallery, which fitted over it, was made so that it but slightly increased the length.

Much ingenuity was expended in devising suitable burners for use with the upright mantle, the chief aim being to ensure a hot steady flame of the right shape with thorough admixture of the air and gas before combustion. Some of these burner heads consisted of open circular slots, others of flat gauze discs with a small baffle in the centre, whilst others were provided with gauze domes and steatite or cut metal tops. All these different varieties, however, suffered from the defect of under-aëration of the gas before combustion, so that a chimney was required in order to create an up-draught and to bring a supply of air from outside the mantle in contact with the burning gas on its surface.

If these burners were used without a chimney, the unburnt gas from the inner zone had to travel a short distance from the surface of the mantle through which it was passing before it obtained the additional air necessary for its complete combustion, with the result that the layer of highest temperature was outside the mantle, which was not in consequence raised to the highest degree of incandescence. When a chimney was used, however, the current of air created by it burnt the gas on the surface of the mantle itself, and the best results were obtained. Burners of this class still form the majority of those employed with upright mantles, and a chimney is a necessity in all burners in which less than one-half the total volume of air needed for the complete combustion of the gas is drawn in, and with a 14- or 15-candle power gas, a 6-inch chimney is generally sufficient to supply the necessary air, whilst with a rich gas a longer chimney is required.

A serious trouble with mantle lighting has been the carbonisation of the mantle, which commences with a slight sooty deposit at one spot, and then rapidly grows over the surface of the mantle, reducing the light emitted and soon destroying the mantle.

When the flame is under-aërated and contains a ratio of less than 2·2 volumes of air to 1 of gas, some methane escapes combustion in the inner zone of the flame, and burns with the carbon monoxide and hydrogen in the outer flame, and it is this which causes the trouble.

On replacing the ordinary tube of a Bunsen burner with one made of platinum, if the ratio of gas and air be so arranged as to give a blue non-luminous flame, on heating the platinum tube the flame becomes luminous, although not to such an extent as would have been obtained from the original gas. If the tube be allowed to cool down, the flame again becomes non-luminous, showing that the luminosity is due to the restoration of heat to the flame and not to any alteration in the composition of the gas. But with a Bunsen burning with a green inn cone, luminosity cannot be produced by heati the mixture of gas and air. On now taking a ordinary Bunsen with a brass tube, and surroun ing the blue non-luminous flame with a platinu gauze cylinder so arranged that the sides of th flame heat it to a high temperature, the top the flame will become luminous, owing to th platinum superheating the flame gases from th inner cone and causing them to decompose wit separation of particles of carbon. The sam result is obtained with an ordinary mantle ope at the top, and it is to this cause that the deposition of carbon on the mantle is due.

Mantle burners in which regeneration ha been attempted have also been tried, but th fact that the air or gas can be heated separatel and then utilised to give a very hot flame, doe not apply to the mixture of the two to an greater extent than is found in the inverte burner, as, when a mixture of air and gas i heated, oxidation of the gas commences, an the loss of combustible matter due to this caus outweighs the advantages of preheating.

Real improvements in the burners employed for mantle heating started in the early nineties, when Chemin and Bandsep began working at the idea of adding air t the gas in small portions so as to gain a mor intimate mixture of the two before combustion and it was the perfecting of this idea in the Kern burner which gave the best chimneyless burner in use.

In this burner, the gas issues from the usual injector into a suction tube, consisting of two cones united at their summits, which increases the proportion of air drawn in with the gas, and the mixture then passes into an enlarged head, where baffling devices ensure thorough mixing, and the burner top is so constructed that the flame of the burning gas is thrown against the mantle, yielding a higher duty than with an ordinary burner and chimney.

The sharp edge of this burner resulted, however, in the mantles having a comparatively short life, and it is being replaced very largely for public lighting by inverted systems.

The visible duty obtained from the incandescent mantle depends largely upon the pressure at which the gas is supplied, and now that its use has become universal, no gas undertaking should, in their own interest, supply gas to consumers at less than 2 inches ($\frac{20}{10}$) pressure, and when centres of high illuminating value are needed to compete with arc lighting for outside work and large buildings, the light which can be obtained from a mantle can be enormously increased by the use of high-pressure lighting, such as the Keith, Sugg, Selas, and other systems, in which either the gas or air is placed under greater pressure than the ordinary, so that by using what are practically blowpipes, a much larger volume of gas is consumed in a given space, and from 30 to 60 candles light obtained per cubic foot of gas consumed.

The quality of the gas has a certain influence on the light given by the mantle, but not as much as is generally supposed. If an ordinary burner and mantle be tested first with 16-candle gas, then with 15, and finally with 14-candle power gas, it is often found that it gives a better light with the 15 than the 16, and a further improvement with the 14-candle gas. This, however, is dependent upon the fact that the burner is drawing in less than the necessary amount of air to give the best conditions of combustion in the inner zone, and that the right degree of aëration is being more and more nearly approached with the poorer gas. When care is taken to ensure the correct ratio of air and gas consumed in each case, it is found that for qualities of gas between 14 and 18 candle power, there is a gain of about 3 p.c. in the light emitted by the mantle for each candle-illuminating power in the gas.

Seldom in the industrial history of the world has any one invention wrought such alterations in a great manufacture as has been the case with the incandescent mantle, which, being perfected just at the time when electricity was threatening the supremacy of gas as an illuminant, entirely revolutionised the gas industry.

Before the introduction of the mantle, the usual quality of the gas supplied was what was known as 16-candle power, and the light obtained from it by the consumer was anything from 7 to 8 candles per cub. ft. with regenerative burners, down to less than 1 candle per cub ft. with small flat-flame burners, whilst with the incandescent mantle from 14 to 60 candles per cub. ft. can be obtained.

LIGHT EMITTED PER CUBIC FOOT OF 16-CANDLE GAS CONSUMED PER HOUR

Burners	Candle units
Incandescent (high-pressure inverted)	35 to 60
,, (high-pressure upright)	30 ,, 35
,, (ordinary inverted)	20 ,, 25
,, (ordinary upright)	14 ,, 22
Regenerative	7 ,, 10
Standard argand	3·20
Ordinary argand	2·90
Union jet flat flame, No. 7	2·44
,, ,, ,, 6	2·15
,, ,, ,, 5	1·87
,, ,, ,, 4	1·74
,, ,, ,, 3	1·63
,, ,, ,, 2	1·22
,, ,, ,, 1	0·85
,, ,, ,, 0	0·59

It was also soon found that, in practice, a much poorer gas gave as good or better results with most incandescent mantle burners, and with the general adoption of the mantle, the candle power of the gas supply has been lowered in nearly every large town in England.

At the present time (1921), the normal annual mantle consumption of the world approximates to:

Great Britain	60,000,000
America	80,000,000
Germany	90,000,000
France	20,000,000
Italy	3,000,000
Belgium	5,000,000
Australia and New Zealand	6,000,000
Russia[1]	3,000,000
India[1]	2,500,000
Egypt[1]	1,000,000
Scandinavia[1]	2,500,000

When Welsbach made the first thoria mantles, thorium salts were obtainable only in very small quantities, and from such minerals as thorite and orangite, but with the demand, new sources of supply were found in many directions, notably the immense deposits of monazite discovered in Travancore (S. India) in 1909, and during the last few years, although the amount of thorium nitrate used has more than doubled, there appears no fear of a shortage hampering the mantle industry.

Many theories have been brought forward to explain the wonderful light-giving power of the mixture of 99 p.c. thoria and 1 p.c. ceria, but none of them explains both the facts, *i.e.* that the maximum light is obtained only in the extreme outer layer of the Bunsen flame, where both air and combustible gases are present, and that it is only with 1 p.c. of ceria in the mixture that it is obtained, a mantle of pure thoria or pure ceria giving practically no light.

The probable explanation is that in the mantle, the thoria, being in a porous condition, is a good non-conductor, and owing to this, to its low specific heat and low power of radiating heat, it can be raised to the temperature of the flame; ceria, on the other hand, has a wonderful power of radiation, as shown by Féry, and has also a catalytic action upon mixtures of combustible gases and oxygen, but its radiation is so great that it cannot be heated in a Bunsen flame to the temperature necessary to give light.

When ceria is added to thoria, the light emitted by the mantle increases until 1 p.c. by weight, or 0·1 p.c. by volume, is present, because the ceria is so insulated by the excess of thoria that it is not only brought up to the temperature of the flame, but by its catalytic power tends to focus the combustion of the extremely attenuated flame gases upon the widely distributed ceria particles, and so raises them to a far higher temperature than the mantle, a temperature, however, which cannot be detected by the thermo-couple, which gives only the average temperature of the mass with which it is in contact, and fails to show the temperature of the 0·1 p.c. of ceria. Addition of more ceria to the mixture causes such a rapid cooling of both mantle and flame by radiation, that the light at once begins to fall; and by the time 10 p.c. of ceria is in the mixture, the mantle gives no more light than a thoria mantle, but a much increased heat radiation.

The analogy between the luminescence of thorium-cerium mixtures when heated (the maximum value being at 1 p.c. ceria, mixtures with 10 p.c. ceria and over being non-luminous), and the phosphorescence of mixtures of pairs of rare earths (say A and B), under the bombardment of cathode rays (where with pure A and more than 20 p.c. B there is no phosphorescence, which, however, reaches a maximum with 0·5 to 1 p.c. of B), is interesting (*see* Urbain, Ann. Chim. Phys. 1909, [viii.] 18, 222–376; Bruninghaus, *ibid.* 1910, [viii.] 20, 519–546; 21, 210–283).

The work of Le Chatelier, Nernst, Schmidt, and others, shows that the thoria-ceria mixture gives light rays rich in blue, green, and yellow, but poor in red, so that the proportion of energy radiated as light at the temperature of the mantle is high.

C. S. G.

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[1] A large proportion in conjunction with high-pressure oil lamps.

GAS, OIL. Even before the introduction of coal gas, it had been found that oil could be decomposed at a temperature a little below 1000° with the formation of gas of high illuminating power, and when coal gas had overcome the prejudice existing against it in the early years of its inception, several attempts were made to utilise oil instead of coal for the production of illuminating gas, but with no commercial success, owing to the price of the oil.

As early as 1815 a patent was granted to John Taylor for an apparatus for the decomposition of oils, which is interesting as being of much the same type as those still employed; whilst in 1819 Gordon and Heard took out a patent for compressing oil gas, and it was in the liquid separated during compression of this gas that Faraday discovered and isolated benzene.

After this period, oil gas appears to have been but little used until in 1871, when it began to be employed for the lighting of railway carriages on the Continent in place of oil lamps, and it was from this that the firm of Julius Pintsch built up their system of railway-carriage lighting, which soon spread throughout Europe and to England and America, and at a slightly later date oil gas began to be employed for lighting country houses and small villages where the consumption of coal gas was not sufficiently great to allow the erection of coal-gas works.

It was also largely adopted, in the compressed condition, for the lighting of buoys and for other purposes where the portability of cylinders containing it under compression fitted it for special uses in spite of its cost.

The oils now used for the production of gas are generally the blue or green shale oils, although slightly better results may be obtained from the Russian so-called 'solar distillate,' which is obtained by subjecting the residues of Russian oil, left after the lamp-oil fractions have been driven off, to further distillation.

Such oils begin to decompose with evolution of gas at a little under 500°, and the effect of the temperature of the retort on the products is shown in the following table [1].—

Oil used	Russian 'distillate oil'
Specific gravity	0·864
Flash-point	149°F.=65°C.

Temperature of retort	500°	700°	900°	1000°
Cubic feet of gas per gallon . . .	12	60	72	84
Percentage of residuals	59·1	22·7	12·7	11·8
Illuminating power, candles per cub. ft. .	54·8	50·7	57·1	42·2
The gas contains, p.c.:				
Unsaturated hydrocarbons . . .	39·13	36·56	36·55	22·04
Saturated hydro-carbons . . .	42·41	49·45	49·45	54·83
Hydrogen . .	13·58	6·26	11·86	21·54
Acetylene . .	0·052	0·084	0·38	0·46

DISTILLING POINTS OF THE RESIDUES FROM RUSSIAN 'DISTILLATE OIL,' EXPRESSED IN PERCENTAGES OF ORIGINAL RESIDUE. TEMP.=°C.

Temperature	100°–110	110°–120°	120°–125°	125°–130°	130°–135°	135°–140°	140°–150°	150°–160°	160°–170°	170°–180	180°–190°	190°–200	Sp. gr.	Flash-point
														F.
Original oil .	—	—	—	—	—	—	—	—	—	1	1	1·5	0·864	149°
Residue after decomposing at:														
500° . .	—	—	—	—		—	4	3·5	0·5	2·5	3	2	0·866	58°
700° . .	—	—	9	1	2	1·25	9·5	4	1·5	3·5	3	2	0·908	Below 32°
900° . .	1·6	5	3·3	3·3	5	3·3	6·6	5	6·6	5	—	—	0·926	Below 32°
1000° . .	—	—	—	—	—	—	10	1	2·5	2	Nil	1	1·019	40°

On decomposing the oil at 500°, the gas is small in quantity and white in colour, the hydrocarbons being present almost entirely as vapours, a large proportion of which go forward with the gas and condense in the holder, so that the 59 p.c. of residuals condensed in the receiver do not represent the total condensible hydrocarbons.

After condensation of the vapours, the gas amounts only to 12 cub. ft., and contains the saturated and unsaturated hydrocarbons in nearly equal proportion, whilst on examining the tarry residuals it is found that the flash-point is considerably lower than that of the original oil, and also that 15·5 p.c. distils over below 200°, whilst with the original oil only 3·5 comes over below that temperature.

On decomposing the oil at 700°, the yield of gas is increased to 60 cub. ft. per gallon of oil used, and is of a buff colour. In the gas the unsaturated hydrocarbons are 2·5 less in quantity than in the former case, and there are more saturated hydrocarbons. On examining the residuals, the effect of the increase in temperature is found to be most marked; they have decreased in quantity from 59·1 p.c. to 22·7 p.c. of the original oil decomposed, whilst the flash-point has fallen below the freezing-point, and 36·75 p.c. of the residuals distils below 200°. Nine p.c. of the residuals distil at 123°–125°, whilst 9·5 p.c. distils at a temperature of 140°–150°. At 900° the decomposition of the oil yields a still larger volume of gas, in which the percentage of unsaturated hydrocarbons is the same as before, but there is a large increase in the quantity of saturated hydrocarbons, and a slight increase also in the illuminating value of the gas.

The residuals, at this temperature, fall to 12·7 p.c. of the oil used, and on fractionating them more than 1 p.c. distils at 100°, and 5 p.c. at a little over 110°.

On now raising the temperature to 1000°, another increase takes place in the volume of the gas, 84 cub. ft. being obtained per gallon of oil decomposed, and the illuminating power falls from 57 to 42. On analysing the gas, it is found that the percentage of saturated hydrocarbons has slightly increased, whilst the percentage of hydrogen has risen from 11·86 to 21·54; on the other hand, the unsaturated hydrocarbons have fallen from 36·5 to 22 p.c. The gas as it leaves the retort has lost its rich chocolate-brown colour, and has become 'sooty' from separation of carbon, and this, as well as the increase in hydrogen, shows that the temperature has been forced to a point at which some of the hydrocarbons, and mainly the unsaturated hydrocarbons, have been decomposed.

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[1] Lewes, J. Soc. Chem. Ind. July 30, 1892.

The residuals collected from the gas made at this temperature are of nearly the same volume as those obtained by decomposing the oil at 800°, but differ from them in containing nothing with a lower boiling-point than 140°–150°.

From the results obtained in practical working, 900° has been generally adopted as the best retort temperature to employ, whilst the kind of oil used is generally governed by local conditions. The following table gives the results obtained with various grades of oil:—[1]

Name of oil . .	'Lustre'	Solar distillate	Shale oil	Shale oil
Sp.gr. . . .	0·826	0·8656	0·8495	0·854
Colour . . .	Water white: bluish fluorescence.	Reddish brown: green fluorescence	Reddish brown: greenish fluorescence.	Reddish brown: green fluorescence.
Fractional distillation	1st drop 115°	1st drop 110°	1st drop 225°	1st drop 250°
	5 p.c. 140	4 p.c. 170	5 p.c. 248	5 p.c. 275
	10 ,, 146	10 ,, 238	10 ,, 255	10 ,, 285
	15 ,, 152	15 ,, 246	15 ,, 260	15 ,, 288
	20 ,, 172	20 ,, 252	20 ,, 270	20 ,, 295
	25 ,, 176	25 ,, 255	25 ,, 275	25 ,, 300
	30 ,, 190	30 ,, 267	30 ,, 280	30 ,, 320
	40 ,, 205	35 ,, 271	35 ,, 286	35 ,, 335
	45 ,, 212	40 ,, 276	40 ,, 290	40 ,, 350
	50 ,, 217	50 ,, 285	45 ,, 294	
	55 ,, 224	55 ,, 291	50 ,, 316	
	60 ,, 230	60 ,, 320	55 ,, 350	
	65 ,, 234	65 ,, 345	Thermometer rising rapidly	
	70 ,, 243	Thermometer rising rapidly		
	75 ,, 255			
	80 ,, 262			
	85 ,, 270			
Best results:				
Gas per gal. . .	74·5 cub. ft.	82·9 cub. ft.	82·5 cub. ft.	66·6 cub. ft.
Illuminating power.	49·6 candles	48·2 candles	41·2 candles	62·9 candles

The form of retort and the general apparatus used vary slightly in the processes introduced by Keith, Patterson, Pintsch, and Pope, but a description of the Pintsch plant will suffice to make clear the general principles upon which they all depend.

The retorts are of iron, D-shaped and 10 inches high by 6 feet in length. They rest upon fire-brick, one above the other (Fig. 1), and are connected vertically in pairs. The lid of the upper retort is provided with a siphon pipe, fitted with a funnel at the end into which oil is allowed to flow from an overhead tank, the rate of flow being capable of adjustment by a micrometer cock. The other end of the siphon is continued inside the retort for about 12 inches, and discharges the oil on to a loose thin sheet-iron tray, about 2½ inches deep, which occupies the whole length of the retort, and which is changed and cleaned about once a week. The oil is heated and vaporised in the first retort, and the vapour passes from the further end of the retort downwards into the lower retort, which, being directly over the furnace, is considerably hotter than the upper, the temperature of the retort being a full cherry-red. Here the vapours are 'cracked' and rendered permanently gaseous, and after passage through this retort, they are led by a descension pipe to the hydraulic main. The retorts in the bench are fitted with a test cock, by which the colour of the gas can be ascertained, as this acts as a guide to the work the retort is doing. The gas should be of a pale straw colour; if darker, it is assumed that the temperature is too high, and either the heat of the furnace is slightly reduced, or a little more oil allowed to flow in. Each pair of 10-inch retorts is capable of making 450 cub. ft. of gas per hour.

The tar from the gas-oil retorts having proved to be of little or no value, from time to time attempts were made to do away with the production of liquid residuals as far as possible in the manufacture of oil gas, so that a deposit of pitch or carbon only should be left in the retort. In 1846 Hilary tried to attain this end by placing condenser tubes above the retort, with a view to returning any liquid that condensed back to the retort, where it would be subjected to further distillation, the ultimate products being gas and carbon only. This idea was improved by W. Young, in his process for the manufacture of oil gas.

In Young's process the oil gas, which is obtained by retorting the oil at a moderate temperature, is washed by the oil which is flowing into the retort, and in this way all condensible vapours are removed, and only permanent gases allowed to pass forward to the purifier. As the oil which has served for the washing is employed for the manufacture of the gas, any permanent gases that may have been absorbed are driven out from it during the retorting, and consequently are not lost.

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[1] E. Llewellyn Price, Proc. Incorp. Instit. Gas Eng. 1892.

The retorts are of cast iron and about 10 feet in length, set so as to slope downwards to the back; mouthpieces and ascension pipes are fitted in the usual way, and each mouthpiece has a small cock for testing the colour of the gas, which should be of a pale straw colour, any deeper tint indicating too high a temperature and undue decomposition of the oil. The inflowing oil is admitted through a small tap about 2 feet up the ascension pipe, and drops through the ascending gas on to a steel plate which extends about 3 feet into the retort, thus obviating the direct impact of the oil on to the bottom of the retort. The temperature employed is between 800° and 900°. From the ascension pipes, the gas passes to the hydraulic main at the back of the retort bench, then through a horizontal condenser to the scrubber and finally to the holder. The oil cistern is situated above the scrubber, and the oil can be led through all or any of the sections of the scrubber, after which it passes along the bottom of the horizontal condensers to the hydraulic main. From the hydraulic main it enters a small cistern fitted with an indicating float, by which the flow of oil into the retort can be regulated. It will be seen that in this system the oil is always travelling in an opposite direction to the flow of gas.

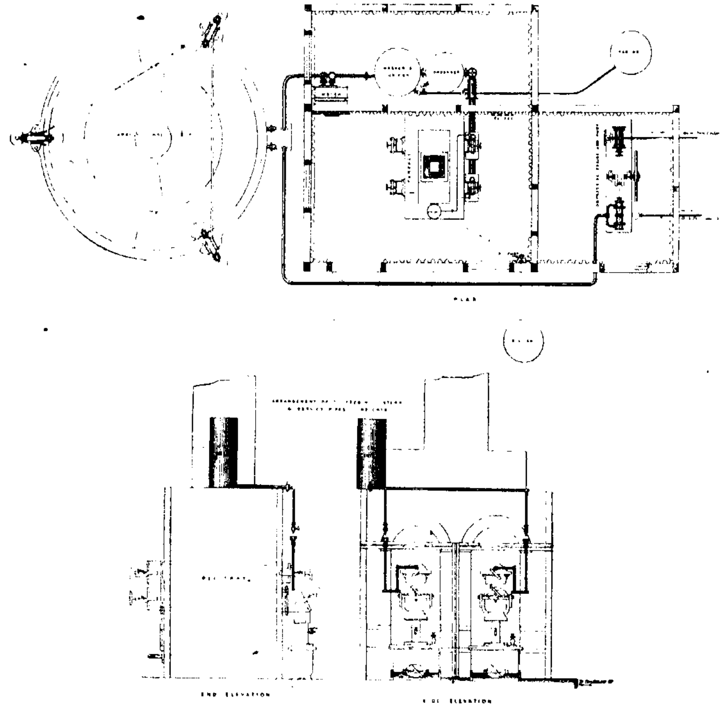


FIG. 1.

The oil used is 'blue shale oil' with a specific gravity of about 0·850. Each retort makes 500 cub. ft. of gas per hour, and 5¼ cwts. of a very dense graphitic coke is left in the retort for each ton of oil decomposed. When tested on the photometer in burners most suited for its combustion, the gas gives an average of 60 candle power.

The composition of the gases made by the ordinary and by the Young process is shown in the following analyses, the ordinary oil gas being of 50 candle power, and the Young gas 60 candle power:—

	Ordinary	Young
Unsaturated hydrocarbons	33·16	43·83
Saturated hydrocarbons .	45·15	36·30
Hydrogen	19·65	16·85
Carbon dioxide . . .	0·50	0·63
Carbon monoxide . . .	0·50	0·00
Oxygen	0·60	1·14
Nitrogen	0·44	1·25
	100·00	100·00

In using oil gas for lighting railway carriages and buoys, the gas is forced at six or seven atmospheres pressure into receivers which, in the case of railway carriages, are fixed to the under frame of the carriage. These receivers are connected with a governor, which reduces the pressure of the gas passing through it to 1 or 2 inches of water, at which pressure it is led to the lamps in the carriage roof. The gas is burnt at specially made flat-flame nipples, consuming about a foot of gas per hour, and at this rate yields a light of about 8 candles per burner.

Improvements have been made from time to time by the introduction of horizontal flat flames in place of upright flames, by the use of small regenerative burners, and also by increasing the illuminating value of the oil gas by admixture with acetylene, but the greatest advance that has been made is due to the utilisation of oil gas in the incandescent mantle, which was introduced into this country for railway lighting in 1904. Until the inception of the inverted incandescent mantle, its use for such a purpose as railway lighting was not very successful, as the vibration rapidly destroyed the mantle, and the light, being thrown in an upward direction, necessitated the use of reflectors. With the introduction, however, of the inverted mantle, it was found that the suspension of the mantle on its frame, which merely rested on catches forming part of the nozzle of the burner, acted as a satisfactory anti-vibrator, rendering the mantle far less liable to be effected by shock, whilst in the event of an unusually violent jar breaking it, it is still held in position by a wire cage, which keeps it in contact with the flame, and ensures a light until the mantle can be replaced.

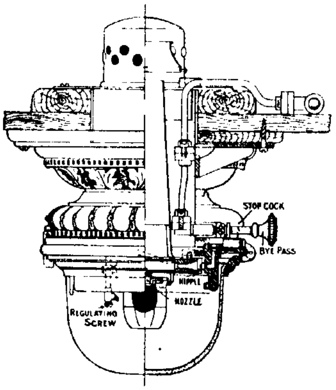
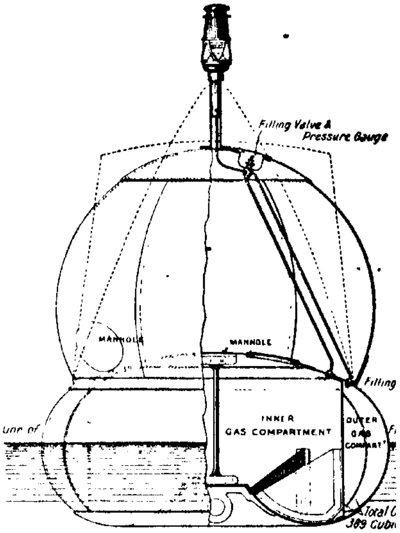


Fig. 2.

The high calorific value of oil gas, which averages 1000 B.Th.U. per cub. ft., or double that of London coal gas, enables it to be burnt in very small atmospheric burners and mantles, so that a consumption of 0·6 cub. ft. per hour gives 24 candles of illumination, thus trebling the efficiency of the lighting, whilst nearly halving the consumption.

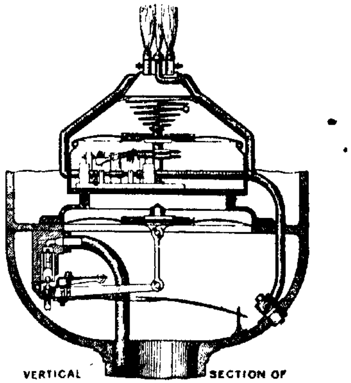
Fig. 2 shows the arrangement of the lantern and burner as used for railway-carriage lighting, whilst Figs. 3 and 4 show the general construction of gas buoys and burners showing a flash light.

As already mentioned, when oil gas is compressed into the receivers at a pressure of about 100 lbs., about a gallon of liquid hydrocarbons separates from 1000 cub. ft. of gas, occasioning a fall in illuminating power of about 10 candles. This is also observed, but to a smaller extent, in compressing a rich coal gas. This liquid contains as its main constituents

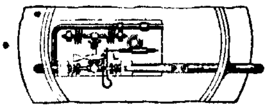


GAS-BUOY PINTSCH'S SYSTEM

Fig. 3.



VERTICAL SECTION OF GAS REGULATOR & FLASHING APPARATUS



PLAN OF FLASHING APPARATUS

Fig. 4.

benzene, toluene and hydrocarbons of the ethylene (C_nH_{2n}) group up to normal heptylene, together with some naphthenes and very small quantities of other benzenoid hydrocarbons.

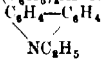
The tar formed during the ordinary process of manufacturing oil gas amounts to about 5 gallons for each 1000 cubic feet of gas. But little use has been found for it. It contains only very small quantities of phenols or basic constituents. In most cases, it is burnt beneath the retorts. One of the chief points in Young's process of making oil gas was that the tar is entirely got rid of, and a very dense and valuable form of carbon obtained instead. V. B. L.

GAS, PRODUCER. *v.* FUEL AND GAS, WATER.

GAS WARFARE. The first attempt to use poison gas in modern warfare was made by the Germans in April, 1915, when they liberated large quantities of *chlorine* from cylinders of the liquefied gas in the Ypres salient. An efficient protection against it consisted of pads of cotton wool or a flannel bag soaked in solutions of sodium thiosulphate and carbonate, contained in a helmet fitted with a mica window. Subsequently, in December, 1915, the Germans made use of *phosgene* gas, for which sodium phenate, mixed with hexamethylenetetramine, contained in a box respirator, was found to be a suitable protection. 'Activitated' charcoal, or charcoal and alkaline permanganate, have also been employed. Attacks by gas clouds were soon replaced by 'gas shells'—that is, by shells containing toxic materials which could be vapourised or 'atomised' by the explosion. The first to be used was the so-called 'tear' or 'lachrymator' shell containing xylyl or benzyl bromide, afterwards replaced by the highly-poisonous *trichloromethyl chloroformate* $ClCOOCCl_3$; by the 'mustard gas,' *dichlorodiethyl sulphide* $(CH_2ClCH_2)_2S$, which has no immediate effect upon the eyes beyond a slight irritation, but produces extremely painful after-effects; the eyes swell and blister, the nose discharges freely, and coughing and vomiting occur. Direct contact with the skin also produces blistering, and the concentrated vapour penetrates clothing.

In addition to these substances, the Germans at various times made use of *phenyl carbylamine chloride*, a 'lachrymator'; *diphenyl-chloroarsine*, a 'sneezing gas'; *allyl iso-thiocyanate*, *brominated methyl-ethyl-ketone*, *dibromo-ketone*, *chloropicrin*, *dichloro-methyl-ether*, and *sulphur trioxide*. In hand-grenades they employed *bromo-acetone*, *bromine*, *chloro-acetone*, *chlorosulphonic acid*, *dimethyl sulphate*, and *methylchloro-sulphonate* (Auld, J. Wash. Acad. Sci. 1918, 8, 45; J. Soc. Chem. Ind. 1918, 127, R).

The following table, from Moureu's La Chimie et La Guerre (Masson et Cie, Paris), gives a list of various toxic substances used by the Germans, with their physiological properties, and the dates of their first employment.

Date when first used on the field of battle	Name of substance	Chemical formula	Physiological action
1915			
April . . .	Chlorine (gas)	Cl_2	Suffocating
June	Bromine (liquid)	Br_2	Suffocating
June	Benzylbromide (liquid) . .	$C_6H_5—CH_2Br$	Lachrymatory
July	Bromoacetone (liquid) . . .	$CH_3—CO—CH_2Br$	Suffocating, lachrymatory
August . . .	Methyl chloro-sulphonote (liquid)	$SO_2<\begin{array}{l}Cl\\OCH_3\end{array}$	Suffocating
August . . .	Chloromethyl chloroformate (liquid)	$Cl—COOCH_2Cl$	Suffocating
August . . .	Bromomethyl ethylacetone (liquid)	$CH_3—CO—CHBr—CH_3$	Suffocating, lachrymatory
1916			
July	Trichloromethyl chloroformate (liquid)	$Cl—COOCCl_3$	Suffocating
December . .	Phosgene (gas)	$COCl_2$	Suffocating
1917			
May	Chloropicrin (liquid) . . .	CCl_3NO_2	Suffocating, lachrymatory
July	"Mustard gas" (ypérite) (liquid)	$S<\begin{array}{l}CH_2.CH_2Cl\\CH_6.CH_5Cl\end{array}$	Suffocating, lachrymatory, vesicant
September . .	Diphenylchloro-arsine (solid) . Phenyldichloro-arsine (liquid).	$(C_6H_5)_2AsCl$ $C_6H_5AsCl_2$	Suffocating, sternutatory
September . .	Phenylcarbylamine chloride (liquid)	$C_6H_5N:C:Cl_2$	Nauseous and toxic
1918			
April	Ethylarsine dichloride (liquid)	$C_2H_5AsCl_2$	Toxic, sternutatory
April	Ethylarsine dibromide (liquid)	$C_2H_5AsBr_2$	Toxic, sternutatory
June. . . .	Diphenylarsine cyanide (solid)	$(C_6H_5)_2AsCN$	Sternutatory
September . .	N-Ethylcarbazol (solid) . .	 $\begin{array}{c}C_6H_4—C_6H_4\\ \diagdown\quad\diagup\\ NC_2H_5\end{array}$	Sternutatory

GAS, WATER, is the term applied to the impure gaseous mixture of hydrogen and oxides of carbon formed when steam is passed through incandescent carbon, an action which was probably discovered by Fontana in the eighteenth century, and was undoubtedly known to Lavoisier who, in 1793, noticed that when steam was passed over incandescent carbon, hydrogen and carbon monoxide were produced.

The first attempt to utilise water gas on a commercial scale dates back to 1824, when Ibbotson sought to increase the volume of gas distilled from his retorts by injecting steam into the red-hot coke remaining at the end of the period of carbonisation. This idea has been revived on many occasions, but so long as the horizontal retort remained in general use for the purpose of distilling coal, the process was found to be impracticable. With the introduction of the vertical retort, however, the system of 'steaming' was again experimented with, and has now been fairly generally adopted with a good deal of success. The original practice of admitting the steam to the retort when the greater part of the coal gas has been evolved has given way to the more effective method of admitting a restricted quantity during the whole period of distillation.

The extent of the water-gas industry in this country is shown by the statistics issued by the Board of Trade, which indicate that annually approximately 24,000 million cubic feet are generated. The number of gas works producing the gas is 148, of which 101 are companies, and 47 undertakings belonging to local authorities. The world's output of water gas is in the neighbourhood of 120 million cubic feet per annum.

When steam is passed through a mass of heated carbonaceous material, the composition of the gas formed will vary with the temperature, and, to a less extent, with other factors, such as the rate of flow and quantity of steam.

It is found by experiment that at temperatures about 600° the reaction is mainly :

$$C+2H_2O=CO_2+2H_2$$

the quantity of carbon monoxide being small, whilst when 1000° is passed, the reaction more nearly approaches $C+H_2O=CO+H_2$.

The products obtained vary with the temperature of the carbon in the following manner :

Temperature of carbon	Percentage composition of resulting gas		
	Hydrogen	Carbon dioxide	Carbon monoxide
600°	66	30	4
700°	65	29	6
800°	62	23	15
900°	54	7	39
1000°	50	2	48

The value of water gas as a fuel largely depends on keeping the percentage of carbon dioxide and nitrogen as low as possible, and it is clear, therefore, that the temperature of the carbon in whatever form it is used, must be kept at or above 1000°, and that a fall in temperature below 900° causes a large increase in the carbon dioxide.

It is also important, in order to keep down the percentage of carbon dioxide, to avoid any excess of steam over the quantity that can be decomposed by the red-hot carbon, as at temperatures above 900° some of the carbon monoxide is oxidised by steam to carbon dioxide, according to the equation :

$$CO+H_2O=CO_2+H_2$$

a reaction, which, being reversible, is never completed, but which causes a serious increase in the volume of carbon dioxide in the water gas if an excess of steam be present.

If, however, the temperature in the generator be maintained as high as possible throughout the gas-making 'run,' and if the volume of steam is carefully adjusted, in practice a water gas is obtained with approximately the following composition :—

Hydrogen . . .	52·0	p.c.
Carbon monoxide . .	38·5	by volume
Carbon dioxide . .	4·5	,,
Methane . . .	1·0	,,
Nitrogen . . .	4·0	,,

Theoretically, methane should be absent, but owing to the impossibility of obtaining coke entirely free from hydrocarbon bases, a small proportion is always present. It is possible, too, that catalytic action may account for a small quantity of this gas. In addition, sulphuretted hydrogen is evolved to the extent of about 120 grains per 100 cubic feet (0·02 p.c. by volume), while other gaseous sulphur compounds, chiefly carbon disulphide, are present in quantities amounting to from 10 to 15 grains per 100 cubic feet. These impurities, however, are largely dependent upon the proportion of sulphur in the original coke employed.

The systems which have been introduced for the purpose of manufacturing water gas may be classified under the following headings :—

(1) The Continuous System.
(2) The Intermittent System.
(3) The Neat-Oxygen System.
(4) Complete gasification of coal and coke in one operation, whereby a mixture of coal gas and water gas is obtained.

Early attempts to manufacture water gas by a continuous process in which steam was passed through coke contained in an externally heated generator failed for the reason that to make water gas successfully the coke must be maintained in a state of incandescence. Since the decomposition of the steam absorbs more heat than is emitted in the formation of the water gas, the coke charge cools more rapidly than the heat can be imparted to it through the fire-clay walls of the generator. Accordingly, when the temperature falls, the carbon dioxide is formed in such quantities as to render the process uneconomical.

In 1849 Gillard introduced a process in which he adopted the entirely new idea of raising the temperature of the carbonaceous fuel by blowing air on to it instead of heating it in a retort fired from without; having raised the fuel to incandescence by its own partial combustion, he then shut off the air supply and passed steam through the fuel, until the temperature was so reduced as to necessitate a fresh blowing up by air. It is this principle of 'blow and run' which has since been employed in all the water-gas processes which have had any claims to success.

After Gillard's time, numerous other attempts were made to introduce water gas, but nothing of importance was done until 1875, when Lowe and Tessié du Motay, in America, inaugurated the present carburetted water-gas systems.

A scientific, and probably a not impracticable, system is that embodying the use of neat oxygen. The process is operated on continuous lines, and results in a gas practically free from nitrogen, but containing 60–70 p.c. of carbon monoxide. Steam is admitted to the base of the generator in the ordinary manner; and along with it is passed a stream of pure oxygen In this way, whilst steam is combining with a portion of the carbon to form water gas, the heat lost by the endothermic nature of the reactions is replaced by the exothermic combination of the oxygen with part of the carbon. If steam and oxygen are regulated in accordance with theoretical requirements the process will proceed with little trouble. R. P. Pictet has recently proposed to employ such a mixture, which is admitted through a tube of refractory material into the centre of the charge in the generator in such proportions that the temperature of the charge is maintained at about 1600°. Practically pure water gas is drawn off and is scrubbed and stored in the usual way.

The fact that water gas contains over 90 p.c of combustible gases, whilst the ordinary producer gas contains only 30 p.c., soon attracted the attention of some European engineering firms, who required an intense heat for welding purposes, and in the early eighties several plants were installed in Europe for welding tubular boilers and other work of the same character.

From a historical point of view, it is interesting to note that the generator then employed consisted of a cupola furnace, about 20 feet in height and 7 feet in diameter, lined with fire-brick, with a constriction a short distance above the hearth, the fire-brick being protected at this point by a water-cooled ring. An air blast was admitted below the water-cooled ring, and in about 10 minutes the ignited fuel was raised to incandescence. The air blast was then cut off, steam was admitted above the top of the fuel, and passing down through it, became converted into water gas, which escaped by the same opening as that through which the air blast was admitted, this being opened and closed by means of a water-cooled slide valve of such construction that it was impossible for any explosive mixture of water gas and air to be formed. The water gas passed on to purifiers, which removed sulphuretted hydrogen and carbon dioxide, and the gas was then stored in gas holders. The fuel was fed into the generator at the top, which was closed by a cone; the whole of the steam, air, and water-gas pipes being governed by an arrangement of lever valves which rendered any explosive mixture impossible. This form of apparatus was installed at the Leeds Forge in 1887.

The impure mixture of hydrogen and carbon monoxide made by such processes burns with a blue non-luminous flame, and is technically known as 'blue water gas,' to distinguish it from the mixture of water gas and oil gas which, introduced in America in 1875, had achieved a great success, and was largely used as a substitute for coal gas under the name of 'carburetted water gas.'

The increase in the price of cannel coal led English gas managers, in 1889, to turn their attention to the American practice of mixing carburetted water gas with the coal gas in order to raise its illuminating power. The process was adopted by the Gas Light and Coke Company, and is now used as an auxiliary to coal gas in nearly every large gas works in Great Britain.

The reasons that prevented the rapid progress of the 'blue water gas,' except for special purposes, are largely to be found in its poisonous properties and the uneconomic conditions of its manufacture at this period.

It has been shown that in the formation of water gas the perfect decomposition would be represented by the equation:

$$C+H_2O=H_2+CO$$

A unit weight of hydrogen in burning to water gives out 34,500 calories, and as 2 units burn to form 18 of water, the heat evolved during its production will be 34,500 × 2 = 69,000 calories: when the 18 units weight of water are again decomposed, this amount of heat will again be absorbed. In this case, however, the water has had to be converted into steam, and so contains an amount of heat equal to the latent heat of steam plus the heat used to raise it to the boiling-point. The latent heat of steam is 536 calories per unit weight of water, and to allow for the heat necessary to bring it up to the boiling-point, this is generally called 600. In the present case, we are dealing with 18 units of water as steam, so the heat present in it will be $600\times18=10,800$ calories, and the extra heat used up in decomposing the 18 units weight of water will be $69,000-10,800=58,200$ calories.

The water having been decomposed, its oxygen is available to burn the 12 units of carbon to carbon monoxide, and as in doing this one unit of carbon emits 2489 calories, the 12 will yield $2489\times12=29,868$ calories. If this be deducted from the previous heat deficit, the result is:

$$\begin{array}{r} -58,200 \\ +29,868 \\ \hline -28,332 \end{array}$$

or a shortage of 28,332 for the 12 units of carbon, or 2361 for one. If the units be taken as lbs., 1 lb. of carbon, in decomposing 1·5 lbs. of steam to hydrogen and carbon monoxide, uses up 2361 calories. In order to obtain this amount of heat, 1 lb. of carbon may be burnt to carbon monoxide by an air blast, so obtaining 2489 calories, so that, theoretically, it should be possible to get the required balance of heat by burning half the fuel by an air blast to producer gas, and by a steam jet converting the remaining half to water gas.

In practice, however, the loss of heat taking place from the escape of the hot producer gas, radiation, &c., necessitates the air blast being continued until a far higher proportion of the carbon in the fuel has been consumed, and by this process, instead of 50 p.c. of the carbon of the fuel being converted into water gas, the actual amount varies in practice from 25 to 30 p.c. In other words, from three to four times as much coke is consumed during the 'blow' as during the gas-making 'run.'

In making water gas by such processes as that which was employed at the Leeds Forge, fuel in the cupola is first raised to incandescence by the combustion of a portion of it under the influence of an air blast, an operation giving as a gaseous product a producer gas of the composition:

Nitrogen	64·5
Carbon monoxide	29·0
Carbon dioxide	4·0
Hydrogen	2·5

A thousand cubic feet of water gas contain, of combustible constituents:—

Hydrogen	2·75 lbs.
Carbon monoxide	30·00 ,,

and the thermal value will be represented by:

$$(2{\cdot}75 \times 34{,}500) + (30 \times 2435) = 167{,}925 \text{ calories}$$

The thermal value of the 60 lbs. of carbon, however, used in making the water gas would be:

$$8137 \times 60 = 488{,}220 \text{ calories}$$

In other words, the water gas formed has only just about 30 p.c. of the heating value of the carbon from which it has been formed, and this loss of 70 p.c. of the calorific value rendered the use of water gas as made by the old European process impossible, save for special purposes.

When, however, the producer gas can be at once led away and burnt whilst hot for any purpose, another 223,328 thermal units will be produced, bringing the total calorific value of the two gases up to nearly 80 p.c. of the value of the carbon used in generating them.

If these conditions could have been satisfied in the early days there is no doubt that water-gas would long ago have been highly successful, but inasmuch as the producer gas is four times greater in volume than the water gas made, and as the gases are produced intermittently and not continuously, the difficulty of utilising both was almost insurmountable, as, if storage had been provided for the producer gas, the gas holder room required would have been enormous, whilst allowing it to cool down would have rendered it hardly worth burning. In some few of the later installations, the producer gas has been successfully used in firing boilers and other work of the same character, and in this way the efficiency of the manufacture of 'blue' gas has been greatly increased.

When the manufacture of carburetted water gas was first successfully carried out by Lowe and Tessié du Motay, it became at once apparent that the producer gas, the loss of which had crippled all water-gas processes, could be utilised in raising chambers filled with chequer brickwork to the high temperature needed to decompose the oils, and so furnish the oil gas which, when mixed with the water gas, rendered the latter luminous. It was, by thus making the carburetted water-gas plant a perfect heat machine, that its greatest success was achieved, as in raising the fuel to incandescence the producer gas, with all its heat in it, was at once burnt with a fresh supply of air in the super-heating chambers, the practical loss of heat taking place throughout the whole apparatus being reduced to a minimum.

In all attempts to make water gas prior to 1896, the incandescence of the fuel was always attained by using the air blast with so deep a bed of fuel that the carbon monoxide and residual nitrogen of the air formed the chief gaseous products. It must be remembered that when 1 lb. of carbon combines with oxygen to form carbon monoxide, as when forming producer gas, only 2489 calories are developed, whilst if air be present in sufficient quantity to burn the carbon completely to carbon dioxide, the amount of heat which is evolved is 3·27 times as great, *i.e.* 1 lb. of carbon gives out 8137 calories.

A process was devised by Mr. Carl Dellwik, in which this fact was utilised by adjusting the air supply, and by keeping the level of the incandescent fuel in the generator at a nearly constant height.

Under these conditions Dellwik claimed that producer gas ceased to exist as a by-product, so that the gases resulting from the 'blow' consisted merely of incombustible products, with a corresponding saving in fuel. It may be said, however, that although in practice the quantity of carbon monoxide present in the 'blow' gases was certainly reduced in Dellwik's plant, it was never possible to obtain a gas entirely free from it. The chief advantage of this type of apparatus was the proportionate increase obtained in the gas-making period owing to the reduction effected in the period of blowing.

In the old 'European' process, it was necessary to blow for nearly 10 minutes to bring the fuel bed up to the right temperature, whilst the period during which the incandescence was sufficiently great to decompose the volume of steam used, limited steaming to 4 or 5 minutes, whereas in the Dellwik process, the period of blowing rarely exceeds 2 minutes, and it is possible to steam for about 7 minutes, much depending upon the nature and condition of the fuel.

The Dellwik generator consists of a sheet-iron shell, lined with fire-brick, which contains the fuel—coke; below the grate level is the valve for the air blast, whilst steam can be admitted either at the top or bottom of the generator. The water gas is provided with two outlets, one at the top and the other at the bottom, connected by a three-way valve. A central stack valve, geared with the air-blast valve, allows the products of the 'blow' to pass away, and through it the fuel is fed into the generator. In practice, the generator is filled to the proper level with coke, which is blown up to incandescence with the air blast, the products passing off through the central stack. When the right temperature is attained, the air is cut off, the central valve being simultaneously closed, and steam is admitted at a carefully regulated rate, which, passing either up or downwards through the coke, is decomposed into water gas. The gas escapes at either of its outlets into a scrubber, where it meets with a stream of water trickling over coke; this cleanses and washes the gas, which is then stored in a holder. When the temperature of the fuel has fallen to a point at which carbon dioxide is formed in excess, the steam is shut off, and the fuel again raised to bright incandescence by the air blast.

Another water gas process, chiefly employed for the manufacture of 'blue' gas, is that due to Kramers and Aarts. This process originated on the Continent, but several installations are now in operation in this country. The novelty in this apparatus consists in having two generators with a regenerating chamber filled with chequer brickwork behind them, so that when the coke in the generators is being raised to incandescence by the air blast, any carbon monoxide that it may contain can be burnt by an extra air supply in the regenerating chamber to heat the chequer work, so that the products escaping up the chimney consist of the products of complete combustion only, and the heat which they contain is further utilised to raise the temperature of the extra air required for the combustion in the generator. When the right temperature of the fuel in the generators has been attained, steam is blown in at the bottom of the first generator, the steam being in excess; the resulting mixture of hydrogen, carbon dioxide, carbon monoxide, and steam is then passed through the regenerator, where it is highly heated, and traverses the second generator, entering at the top and passing downwards through the coke. By this arrangement, the carbon dioxide produced by the excess of steam in the first generator becomes reduced to carbon monoxide, whilst any excess of steam is also decomposed into hydrogen. Inasmuch as in this generator the hottest portion of the fuel will be at the bottom, where the air blast has come more thoroughly in contact with it, the gases finally leave the mass of fuel at the point of highest temperature.

It is well known that when steam is forced in a contrary direction to that in which the air blast has been driven through the generator, the proportion of carbon dioxide is always less than when the steam passes in the same direction as the air blast, and this principle has been used in many forms of generator.

The alterations that have taken place during the last few years in the manufacture of water gas have practically doubled the production of gas per unit weight of fuel used in the generator. The result of several years' practical working at the Leeds Forge with the old 'European' generator, in which during the 'blow' producer gas was formed, gave as an average 34,000 cubic feet of water gas per ton of coke in the generator, but when this was replaced by the Dellwik generator, it was found that the gas coke of reasonable quality and not containing more than 8 p.c. of ash, the yields rose to over 65,000 cubic feet per ton, and under special conditions as much as 70,000 cubic feet could be made.

Gas coke is the fuel most often employed in this country in the generator, and, for effective working, attention should be paid to the size of the coke used. Small sizes can be used only in the smallest generators, and if the coke is too much crushed or contains dust, the dust chokes the air spaces between the pieces of coke and forces the blast and steam to form channels, so lessening the surface of the incandescent fuel exposed to the rapidly flowing gases. At the same time, the coke must not be too large, as that again reduces the surface exposed per cubic foot of generator space. If it is possible to select the size of coke for any ordinary-sized generator, coke which will not pass through a 3-inch mesh, but will pass through a 5-inch, will give an exposure of about 10 square feet per cubic foot of generator space, whilst if the size be reduced so that it will not pass through a 1¼ mesh, but will pass through a 2¼, the surface of fuel exposed is nearly doubled, and a mixture of these two sizes will, with any ordinary generator, give the best results.

The consumption of steam, as found in practice, for the manufacture of water gas, usually amounts to from 27 to 30 lbs. per 1000 cubic feet of gas generated. As regards the quantity of coke used in the generator this varies in accordance with the type of plant in use. With apparatus of the Lowe type a figure of 35 lbs. of coke per 1000 cubic feet of gas is probably the most favourable, but some reduction on this may be expected in those cases where the pan coke is extracted from the generator refuse, and deducted from the total weight of coke shot into the generator. Plants designed essentially for the production of 'blue' gas are generally able to economise in the direction of fuel, and figures so low as 25 lbs. of coke per 1000 cubic feet have been obtained. These figures, as in the case of that given for the Lowe plant, are exclusive of the fuel required in the boilers for steam raising. The steam-raising plant will, with the mixture of breeze and coke usually employed on gas works, require an additional 12 to 15 lbs. of fuel per 1000 cubic feet of gas made.

The cost of manufacturing water gas must, of course, largely depend upon the prevailing value of the raw materials employed, and more especially (in the case of the carburetted gas) upon the cost of the oil utilised. The oil, in fact, in normal times, may represent from 50 to 65 p.c. of the total cost, and for this reason it will be appreciated that the manufacture of 'blue' gas is a very much less costly undertaking than is the case with a carburetted gas. The conditions brought about by the European war were responsible for drastic changes in the degree of carburation which was possible, for whereas, just prior to the outbreak of hostilities, the oil could be obtained for little more than 2*d.* per gallon, it rose, after 3½ years of war, to nearly 1*s.* 6*d.* per gallon. In fact, its scarcity, owing to the shipping position, was such that gas companies throughout the country were rationed in the way of supplies.

The cost of manufacturing carburetted water rose during the war to nearly 2*s.* per 1000 cubic feet, in spite of a reduction in carburation amounting to 50 p.c. That price, however, was largely artificial, and cannot be taken as indicative of normal expenditure. For this reason the analysis of costs prevailing just prior to the war is given on p. 365.

The cost of 'blue' water gas will be practically in agreement with the above after the charges for oil have been deducted, while, so far as residuals are concerned, there will be no revenue from tar. On this basis it will be seen that 'blue' gas costs approximately 8·0*d.* per 1000 cubic feet. As regards capital p.c. In other words, from three to four times as much coke is consumed during the 'blow' as during the gas-making 'run.'

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Thus, with a medium-sized plant, making 8000 cubic feet during a five-minutes' 'run,' the total air passed should lie between 4000 and 5000 cubic feet per minute. Clinkering on water-gas plants must be carried out at frequent intervals, for if once the mass is permitted to accumulate it will gradually arch over in the generator until the latter is almost completely choked. With the Lowe plants it is advisable to perform the operation at intervals of 4 hours, although in cases where a good quality coke is procurable the period may be prolonged to 6 hours.

During recent years there has been some tendency towards the modification of water-gas plant, with the result that in some instances apparatus of a novel character is to be found at work. One such instance is the plant for the production of what is technically known as 'methane-hydrogen' gas, a semi-water gas enriched by means of coal gas tar. One of the most interesting plants, however, which has been erected at a number of gasworks in this country is that which is designed to gasify completely both coal and coke in a single operation. The system was originally suggested by Dr. Strache of Vienna, and has been developed in this country on lines similar to the German process Coal is charged into the upper portion of the generator which in reality conforms to a vertical retort. This coal gradually works its way down the retort, being carbonised meanwhile by a stream of hot water gas issuing from the generator situated at the base of the vessel. The coal should be reduced to the condition of ordinary coke by the time it has passed two thirds of the way down the retort, and it then drops into the water-gas generator Thus, during the 'run' water gas is being evolved from the coke and coal gas from the coal, the two gases intermixing and passing out at the top of the generator. In this way, by the complete gasification of both coal and coke, about 60,000 cubic feet of gas having a gross calorific power of about 380 B.Th.U. per cubic foot may be obtained from a ton of coal.

In addition to being used as an auxiliary to coal gas, blue water gas is applied, with very satisfactory results, to the welding of plates and heating of furnaces and forges; this method has proved of great practical advantage in welding tubes for gas, water, and steam mains, for boiler work, and also for melting steel. Tests conducted by the Admiralty show the strength of a 'blue' gas weld to be equal to that of the plate. Having a very much higher calorific power than producer or suction gas, 'blue' water gas may be used for driving gas-engines, the consumption being about 35 cubic feet per B.H.P. hour. The consumption of ordinary suction gas is about 80 cubic feet per B.H.P. hour. No water gas, however, is entirely satisfactory when used for power, for the large proportion of hydrogen prevents high compression in the cylinder of the engine.

By far the most important property of blue gas is its exceedingly high flame temperature; and Dr. Roessler has found that by admixture with heated air a temperature considerably above the melting-point of platinum may be easily obtained. Under general conditions, however, the temperature of the hottest part of the flame is about 2800°–3000°F. It is owing to this property that blue gas is applicable to such processes as welding, forging, and heating furnaces.

In all processes of the above kind, there is no necessity to purify the gas from sulphuretted hydrogen—merely an ordinary water-scrubber is used. It is, in fact, an advantage to leave the gas unpurified, for it then has a distinct smell, and any escape may be quickly perceived. Thus one of the greatest drawbacks to blue gas—its freedom from smell—is more or less overcome. It will be remembered that in Germany it has, in some cases, been thought advisable to impart a distinct odour to the gas, by passing it through a heavy hydrocarbon oil, such as mercaptan.

A process for which water gas may be employed, and one which will probably be largely developed in the future, is that of producing hydrogen. This is done by liquefying or freezing out all the other constituents—the hydrogen, which, of course, liquefies at a much lower temperature, being left behind, while a more modern method relies on catalytic reaction, by means of which the whole of the carbon monoxide is converted to carbon dioxide. The CO_2 is then readily removed by means of lime or washing with water under pressure.

Cement manufacturers make use of water gas, which is introduced into the revolving kiln for the finishing-off process, and the gas finds its way into the brick-making industry.

A. M.

GASEOUS FUEL *v.* FUEL.

GASES, BLAST FURNACE, *v.* FUEL.

GASTROSAN. Trade name for bismuth bisalicylate.

GAULTHERIA OIL *v.* OILS, ESSENTIAL.

GAULTHERIASALOL. Trade name for methyl salicylosalicylate.

GAULTHERIN *v.* GLUCOSIDES.

GEBLITOL. *Sodium hydrosulphite.* Used as a disinfectant.

GEDDA GUM *v.* GUMS.

GEISSOSPERMINE *v.* PEREIRO BARK.

GELATIN. Gelatin, the purest form of glue (*q.v.*), may be obtained by the action of hot water or of water in presence of dilute acids, on intercellular connective tissue such as the skin, tendons, muscles, &c. Hoofs, bones, intestines, bladders, fishbones, &c., are also made use of for preparing crude gelatin.

According to the process employed by Nelson, the parings, &c., of skins are scored on their surface, and are digested in a dilute soda lye for 10 days. They are then digested at 70°F. in an air-tight, cement-lined vat, and are washed with cold water in a revolving cylinder, and are bleached by means of sulphurous acid gas. After being freed from moisture by pressure, they are digested with water in earthen vessels enclosed in steam chests, and the resultant solution is strained at 100°–120°F. It is then solidified in a thin layer on a marble slab, and is washed free from acid, redissolved at the lowest possible temperature, and dried in thin sheets on nets. According to the process employed by Cox at Gorgie, near Edinburgh, the hides, of which the shoulders and cheeks are preferred, are washed, cut up and pulped by special machinery. The pulp is pressed between rollers, and is mixed with water and heated from 150° to 212°F. A little cow's blood is added to the gelatin solution thus produced, at a temperature not exceeding 170°F., and the solution is further heated, the scum produced by coagulation of the blood albumen being skimmed off. The pure solution remaining is run off and solidified. As prolonged heating impairs the gelatinising power of gelatin, it is preferably dried *in vacuô*.

Several other processes, not differing widely from the above, are also employed. A mixture of vegetable and animal charcoal is sometimes used for purifying dark solutions. Gelatin may also be extracted from bones (which yield one-third of their weight) by causing water to trickle over crushed bones, through which steam is constantly passing (*cf.* GLUE).

Isinglass, the dried swimming bladder of fish, usually contains from 86 to 93 p.c. of gelatin. Russian isinglass is prepared by cutting open and washing the bladder and exposing it to the air with the delicate silvery inner membrane turned upwards. This membrane is stripped off, kneaded in damp cloths and dried. According to Martin, the bladders are first cleansed from blood in hot water, and are cut open and exposed as above, the inner membrane being finally removed by beating and rubbing.

The varieties of isinglass are known by special names dependent on the place of production and their appearance. The Russian varieties are obtained from the sturgeon; Brazilian (sometimes known as Cayenne) from the *Silurus Parkerii*; Manilla and East Indian from an uncertain source. The bladders of cod, hake, and other fish are also employed. *Lump*, *pipe*, and *purse* isinglass are obtained from the unopened bladder, and *leaf* and *honeycomb* from the cut and opened bladder. Long or short *staple* and *book* and *ribbon* isinglass are respectively twisted, folded in packages, and rolled out.

Pure gelatin is an amorphous, brittle, transparent, tasteless, inodorous body, neutral to test paper, and absolutely permanent in dry air. It is heavier than water, and is insoluble in alcohol or ether.

It contains about 50·0 p.c. of carbon, 6·6 p.c. of hydrogen, 18·3 p.c. of nitrogen, and 25·1 p.c. of oxygen. According to Mulder, calcium phosphate is always present. Schlieper finds sulphur in bone and ivory gelatin to the extent of 0·12–0·14 p.c. Von Bibra has also found it in bone gelatin, and Hammersten (J. Pharm. Chim. 9, 273) has found about 0·7 p.c. of sulphur in fine commercial gelatin.

When moist or in solution, gelatin rapidly putrefies, and possesses the characteristic property of becoming acid at the commencement of the change, although ammonia is finally evolved.

When steeped in water, gelatin takes up from 5 to 10 times its weight of water, a sufficient quantity to dissolve it when warmed to 30°. When immersed in dilute HCl, the volume of liquid absorbed and the concentration of anion in the jelly depend, at a given temperature, on the ionisation and concentration of the acid (Procter, Chem. Soc. Trans. 1914, 313).

A solution containing only 1 p.c. of gelatin becomes a jelly on cooling. Prolonged or repeated heating reduces and finally destroys this property, on which the value of gelatin principally depends, so that the preparation is usually conducted at as low a temperature and as rapidly as possible.

Gelatin is soluble in concentrated acetic acid and in mineral acids, and loses its gelatinising power, but the solution forms a powerful cement for glass, &c. Dumoulin's liquid glue consists of a solution of 2 lbs. glue or gelatin in 1 quart of water and 7 ozs. nitric acid (1·355 sp.gr.). Gelatin is also soluble in alkalis, and the solution, as well as the acid solution, is lævorotatory.

Gelatin is precipitated from solution by tannic acid, forming tannate of gelatin, similar in composition to leather, but not capable of employment as a substitute for that material on account of its want of structure. A saturated solution of picric acid completely precipitates gelatin at 8°C. A mixture of saturated picric solution with 4 parts alcohol precipitates other proteins, but not gelatin, and this fact has been applied to a method of estimating gelatin in presence of other proteins (Berrar, Biochem. Zeitsch. 1912, 47, 189).

Gelatin is also 'tanned' by halogens; 10 grams are macerated at 0° in 500 c.c. of chlorine solution in 10 p.c. NaCl, or with 100 c.c. commercial sodium hypochlorite solution diluted to 500 c.c., and containing 2 c.c. hydrochloric acid, when an insoluble compound is formed. Corrosive sublimate also precipitates gelatin, but lead acetates and potassium ferrocyanide have not that power.

By prolonged boiling with hydrolytic agents such as sulphuric acid, gelatin yields a high percentage of glycine—leucine, proline, oxyproline, but no trytophane, cystine, or tyrosine (Levene and Beatty, Zeitsch. physiol. Chem. 1906, 31, 165).

It gives a weak positive Millon's reaction; the xanthoproteic, biuret, and Mollisch's tests are positive; the Adamkiewicz test is negative.

The value of gelatin as a food is somewhat doubtful. Gelatin prepared from bones was largely used by the soldiers and poor of France during the first Revolution, but the idea that its large proportion of nitrogen renders it valuable as a flesh-former appears to be erroneous. It is, however, of limited value as a heat-producer instead of fat and carbohydrates.

Gelatin differs but little in appearance from *chondrin*, which is obtained from cartilaginous tissue, but has a much higher gelatinising power than that substance. Gelatin almost invariably contains chondrin, and, when the proportion of that substance is high, is of considerably less value, especially for the preparation of photographic emulsions, which require a maximum of tenacity.

Chondrin is precipitated from aqueous solution by acetic acid, and is not soluble in excess. Lead acetates, alum, and the sulphates of iron, aluminium, and copper also precipitate chondrin. A rough test for the presence of chondrin in gelatin, useful for photographic work, consists in adding a concentrated solution of chrome alum to a 10 p.c. solution of the gelatin in hot water. If an injurious amount of chondrin be present, the gelatin will set whilst hot. Most photographic gelatins, however, contain but little chondrin.

In judging the value of gelatin, especially for photography, the following properties and tests will be useful: (1) The ash, according to Eder, varies from ½ p.c. in good, to 5 p.c. in inferior, and 10 p.c. in adulterated varieties. According to Abney, however, excellent photographic gelatins sometimes contain as much as 2·5 p.c. (2) A good gelatin will take up from 5 to 10 times its weight of cold water when soaked, *i.e.* sufficient to dissolve it on warming to 30°. (3) The solubilities of gelatins vary considerably. Nelson's No. 1 will dissolve in the ordinary 'cold' water in warm weather, and scarcely sets at 75°F., whereas Coignet's gold label only melts at about 110°F., and sets rapidly. For ordinary photographic emulsions, Abney recommends a mixture of 'hard' and 'soft' gelatins in proportions dependent on the weather, a good mixture containing 1 part of the former to 3 of the latter. (4) The amount of fat in the gelatin should be estimated by precipitating the gelatin by addition of alcohol to the solution. Fatty matters are best removed by skimming the solution or by making a jelly and removing the top. (5) The colour of the solution, the tenacity of a jelly of known strength, and the presence or absence of acid, which is frequently present in sufficient quantity to be distinguished by taste, should also be noted.

Isinglass, although free from chondrin, is not available for photographic purposes on account of its great solubility and inferior tenacity.

Gelatin is largely used for culinary purposes as a vehicle for other materials, and is similarly employed in bacteriology. It is valuable for taking casts and impressions for electrotypy, &c In photography it is employed, in addition to its use for gelatin dry plates, in the carbon process of photographic printing, which depends on the power of potassium dichromate to render gelatin insoluble when exposed to the action of light. This property is also employed in making an insoluble glue or a waterproofing material, by adding dichromate to glue or gelatin just before use.

It is also used in dyeing, for making inking rollers for printing, and as a size for paper making and painting.

For clearing beer, wine, &c., isinglass is much superior to gelatin. This property is said by some to be due to the fine, net-like structure of the former. Coarse Brazilian isinglass is usually employed. It is 'cut' or dissolved in sulphurous or other acid before use.

I. S. M.

GELATIN-DYNAMITE *v.* Explosives.

GELIGNITE *v.* Explosives.

GELOSE *v.* Agar Agar, art. Gums.

GELOXITE *v.* Explosives.

GELSEMINE $C_{20}H_{22}O_2N_2$, a crystalline alkaloid occurring in the root of American wild jasmine *Gelsemium sempervirens* (*Gelsemii*, Radix B.P.; *Gelsemium*, U.S.P.), (Ait.) along with gelseminine and a third alkaloid, the two latter being amorphous and yielding amorphous derivatives (Wormley, Amer. J. Pharm. 1870, 42, 1; Sonnenschein, Ber. 1876, 9, 1182; Gerrard, Pharm. J. 1882–1883, [iii.] 13, 502, 641; Thompson, *ibid.* 1886–1887, [iii.] 17, 805; Spiegel, Ber. 1893, 26, 1045; Cushny, *ibid.* 1725; Goeldner, B. Ph. G. 1895, 5, 330). The roots have been re-examined by Moore (Chem. Soc. Trans. 1910, 97, 2223; 1911, 99, 1231). The third alkaloid, *sempervirine*, is little known (Stevenson and Sayre, J. Amer Pharm. Assoc. 1915, 60).

Properties. Crystallises from acetone in glistening prisms containing 1 mol. of acetone, melts at 178°, and has $[\alpha]_D + 15·9°$ in chloroform. The salts crystallise well, B·HCl, m.p. 300°, small prisms; $B·HNO_3$, m.p. 280°, glistening prisms. Gelsemine hydrochloride is physiologically inactive to mammals, but produces strychnine-like effects in frogs. The characteristic physiological action of gelsemium roots is due to the two amorphous alkaloids, to one of which the name of 'gelseminine' has been applied. In general their physiological action resembles that of coniine; they are highly toxic and also exert a mydriatic action on the eye (Cushny, *l.c.*; Moore, *l.c.*). G. B.

GELSEMIUM ROOT. *Gelsemii Radix*, B.P. The dried rhizome and root of *Gelsemium nitidum* (Michaux).

GEMSBOK BEANS. The bean of *Bauhinia Esculenta*, Burch, used as food in India and in the South-West Protectorate of the Union of South Africa The bean is composed of 48 p.c. of shell and 51 p.c. of kernel and is about ½ to ⅝in. in diameter, the average weight being 2 grms., and that of the kernel 1 grm.

An examination by Bray in the laboratory of the Imperial Institute gave the following results:

	Moisture	Crude proteins	Fat	Carbohydrates	Fibre	Ash	Nutrient ratio	Food units
Husks alone . .	8·5	2·5	0·2	67·2	19·8	1·8	1 : 27·1	74
Kernels alone . .	4·0	32·8	41·6	17·2	1·3	3·1	1 : 3·4	203
Whole beans . .	6·2	18·0	21·3	41·6	10·4	2·5	1 : 5·0	140

The bean is free from alkaloids and cyanogenetic glucosides. A golden yellow limpid oil with a nutty flavour and agreeable taste may be extracted from the kernels, with constants very similar to those of cottonseed oil (Bray, Analyst, 1921, 401).

GEMS *v.* Precious stones.

GEMS, ARTIFICIAL. Almost all the mineral species that find an application in jewellery have been prepared synthetically in the laboratory. These artificial products possess the same chemical composition and physical characters as the natural stones, from which they differ essentially only in their mode of origin. It is therefore necessary to distinguish between artificial (*i.e.* artificially produced) gems and imitation and counterfeit gems: the latter will be treated separately in the article Gems, Imitation and counterfeit.

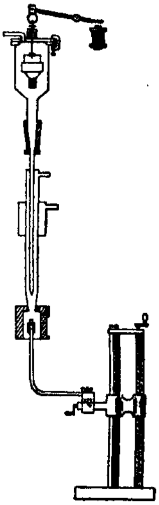
In nature, these extremely hard and intractable minerals have presumably been formed under conditions of high temperature, and pressure during long periods of time. It is therefore not to be expected that crystals of any appreciable size could be produced in the laboratory. The high intrinsic value of the products has, however, offered an incentive to repeated experiments; and the production of corundum of gem-quality and of various colours has now been effected with a high degree of commercial success and in a most unexpected manner. Corundum and spinel are the only gem-stones that have, up to the present, been produced artificially of a size and quality suitable for jewellery.

Diamond has been produced artificially by H. Moissan and others (*v.* DIAMOND); but the many attempts made to induce the common element carbon to crystallise in this form have not resulted in the production of crystals larger than 0·4 mm. across. An interesting account of Moissan's extensive researches in this direction is given in his book Le Four Électrique, 1897 (English translation by A. T. de Mouilpied, The Electric Furnace, 1904).

Corundum was produced artificially first by M. A. Gaudin in 1837, and Frémy and Fiel in 1877 succeeded in producing crystals of fair size and of a fine ruby-red colour (E. Frémy, Synthèse du Rubis, 1891; *v.* CORUNDUM). The largest of these crystals weighed ⅓ carat (0·07 gram), and a few were faceted and mounted as gems; but owing to the extreme thinness of the small platy crystals, they were of no commercial value. About the year 1885 rubies of some size appeared mysteriously on the market, it is said from Geneva: whilst some of these were optically isotropic and softer then true ruby, being of the nature of alumina glass, others were crystalline and identical with natural ruby in their characters. These were known as 'reconstructed rubies,' and had probably been produced by fusing together small natural stones.

In 1902 A. Verneuil (Production artificielle du rubis par fusion, Compt. rend. 1902, 135, 791; Ann. Chim. 1904, [8] 3, 20), who had previously assisted Frémy in his experiments, described a new and eminently successful method for the artificial production of rubies of the finest gem-quality. His apparatus consists of an oxy-hydrogen blowpipe placed vertically, the inner oxygen tube of which is enlarged at its upper end to contain a fine sieve holding the alumina powder used in the process. The periodic tapping on the sieve of a small hammer, actuated by an electro-magnet or a rotating cam, causes a small continuous feed of the alumina powder to fall down the oxygen tube. Beneath the nozzle of the blowpipe is a support terminating in a small rod of fused alumina, the position of which can be adjusted by screw motions. The blowpipe nozzle and the support are enclosed in a box in order to avoid sudden changes in temperature. Hydrogen was used in the early experiments, but in the commercial process coal-gas is used. The flame, with a temperature of 1800°–2000°, must be a reducing one with an excess of hydrogen or carbon. The fine particles of alumina ejected through the nozzle of the blowpipe fall on the alumina support, and, fusing together, build up by accretion a pear-shaped mass, which continues to grow both in height and diameter as the support is gradually lowered.

These pear-shaped masses ('boules') of manufactured ruby ('rubis scientifique,' 'rubis synthétique') grow at the rate of about 12 carats per hour, and they may attain a weight of 80 carats (about 16 grams). One operator can attend to ten or a dozen machines; and the total output in Paris exceeds five million carats (1000 kilos. or about 1 ton) per annum. The price of the uncut material is less than 1*s.* per carat. Now, the curious feature of these masses of fused alumina is that each one of them is a single individual crystal, and not, as might have been expected, an aggregate of crystals or simply an alumina glass. Although the sides of the drop are smooth with a glassy aspect, the rounded end (the last-formed and upper portion in the apparatus) is usually roughened with a fine crystalline reticulation. The narrow stem, where the drop is broken off the support, often shows a bright cleavage surface. The optic axis usually coincides with the axis of the pear-shaped mass, and a section cut perpendicular to this exhibits in the polariscope a typical uniaxial interference-figure. The sp.gr. (3·98–4·0), hardness, dichroism, refractive indices, &c., of this artificial corundum are the same as for the natural mineral. The material further possesses the same transparency, clearness, and rich colours as natural crystals of the best gem-quality. The only means of distinguishing between the two is afforded by certain minute irregularities of internal structure. With a hand-lens or under the microscope, the artificial corundum often, though not invariably, shows minute rounded cavities and curved streaks; whilst in the natural stones the cavities are angular and the streaks are straight.


Verneuil's blowpipe for the artificial production of ruby.

When the material supplied to the Verneuil blowpipe consists of pure alumina powder (prepared by precipitation with ammonia from pure ammonium alum), the crystallised product is perfectly colourless and clear ('white sapphire'). In the early experiments, powdered natural ruby was used as the material. The best ruby-tint is given by the addition of 2½ p.c. of chromic oxide (homogeneously mixed with the alumina by precipitating the two together from a mixed solution of ammonium alum and chromium alum). Smaller proportions of chromic oxide produce a lighter shade of red or pink, and such artificial gems have been erroneously called 'scientific topaz.' The addition of nickel oxide produces a rich yellow colour. Cobalt oxide will not produce a blue colour with alumina alone, but a fine blue is obtained when some magnesia (or lime) is present (L. Paris, Compt. rend. 1908, 147, 933; A. Verneuil, *ibid.* 1059); but now the product, instead of being corundum, is the cubic and optically isotropic mineral *spinel* ($MgAl_2O_4$). Attempts to produce a blue corundum (*i.e.* sapphire) had repeatedly failed until it was obtained by A. Verneuil (Compt. rend. 1910, 150, 185) by the addition of titanic oxide (TiO_2, 0·5 p.c.) and magnetic oxide of iron (Fe_3O_4, 1·5 p.c.). Analysis of this artificial sapphire gave: Al_2O_3, 99·83–99·85 p.c.; TiO_2, 0·11–0·13 p.c.; Fe_2O_3, trace; sp.gr. 3·977–4·01 (A. J. Moses, Amer. J. Sci. 1910, 30, 271). A peculiar stone which has been sold as 'synthetical alexandrite,' exhibits, like the true alexandrite (a variety of chrysoberyl, $BeAl_2O_4$), a green colour by daylight and a red colour by lamp-light, this is in reality artificial corundum, and the change in colour may be attributed to the presence of colloidal chromic oxide (as suggested in the case of alexandrite by O. Hauser, Zeitsch. angew. Chem. 1910, 23, 1464).

References.—In addition to the papers by Verneuil and others quoted above, *see* J. Boyer, La synthèse des pierres précieuses, Paris, 1909; R. Brauns, Über künstliche Edelsteine, Aus der Natur. Jahrg. 1908-9, 647; 1909, 51; J. Escard, Les Pierres précieuses, Paris, 1914.

On the artificial production of minerals in general, *see* L. Bourgeois, Reproduction artificielle des minéraux, Paris, 1884 (Encycl. chim. de Frémy); P. Tschirwinsky, Reproduction artificielle de minéraux au XIX^e siècle, Kieff, 1903–1906. L. J. S.

GEMS, IMITATION AND COUNTERFEIT.

As pointed out in the preceding article, it is necessary to distinguish between artificial (*i.e.* artificially produced) gems and imitation and counterfeit gems. Owing to their rarity and high value, gem-stones have been imitated in various kinds of material since very early times. For instance, although a few of the ancient Egyptian scarabs were cut in genuine turquoise, the great majority of them were made of a blue pottery or faience; and amongst the Romans, coloured glass was used for the imitation of the various transparent coloured gem-stones.

The material most extensively used for the manufacture of imitation gems is a heavy lead (flint) glass known as *paste* or *strass.* This is prepared by fusing in a crucible a mixture of powdered rock-crystal (SiO_2, 38–59 p.c.), red lead (Pb_3O_4, 28–53 p.c.), potassium carbonate (K_2CO_3, 8–14 p.c.), together with a small proportion of borax, white arsenic, or saltpetre. Different recipes vary widely; the amount of lead present depending on the refractive index of the gem to be imitated. A dense flint-glass of sp.gr. 3·54 (*i.e.* about the same as diamond) has $n_D=1·6118$ and dispersion $n_{G'}-n_{A'}=0·0315$; and an extra-dense flint-glass of sp.gr. 5·004 has $n_D=1·7784$ and dispersion $n_{G'}-n_{A'}=0·0568$ (the corresponding values for diamond being 2·4173 and 0·0574 respectively). Optical values still higher are obtained by replacing the potassium by thallium; the sp.gr. of a thallium-lead glass may be as high as 5·6. To obtain the best results in the manufacture of strass, the materials employed must be quite pure; and the fusion carefully conducted, in order to avoid bubbles and streaks. Imitation diamonds (so-called 'Parisian diamonds,' &c.) are cut from the colourless paste. To prepare coloured pastes the colourless paste is powdered, intimately mixed with various metallic oxides or other substances, and again fused. A blue colour is obtained with cobalt oxide; green, with cupric oxide or chromic oxide; red, with cuprous oxide, gold chloride, or purple of Cassius; yellow, with silver chloride, antimony oxide or red antimony, or (in leadless glasses) with coal and a little manganese oxide; black, with tin oxide, manganese oxide, and hammer-slag. An opaque white glass, or enamel, is obtained by the addition of tin oxide, calcium phosphate, or bone-ashes; this may be suitably coloured to imitate opaque stones (*e.g.* turquoise) by the addition of metallic oxides.

These glasses often afford very clever imitations of the various precious stones, resembling them so closely, indeed, that without examination they may be readily mistaken for the genuine article. They are, however, all remarkable for their low degree of hardness, less than that of ordinary window-glass, and they can be readily scratched with a knife. In course of time, they display a dark leaden tarnish on their surface, and when worn in jewellery their edges become rubbed and chipped. When examined with a magnifying-lens, bubbles and streaks are often to be seen in them. Optically they are isotropic and lacking in dichroism.

To avoid the effects of abrasion in wear, and also no doubt as a deception in case the test of hardness is applied, these soft materials are sometimes faced with a harder material such as rock-crystal or colourless topaz. In the *doublet,* the upper portion, above the girdle, consists of this harder, colourless material, while the lower portion, protected in the setting, consists of coloured strass which imparts its fine colour and brilliancy to the whole. The *triplet* consists of an upper and a lower portion of harder material, with a layer of the coloured strass between. Such counterfeits can, of course, be readily detected when the unmounted gem is viewed sideways, but when it is mounted in its setting detection is not so easy. Doublets and triplets are also built up of genuine stones, with the object of improving the colour, and of producing a gem of larger size.

Another kind of fraud sometimes practised with precious stones is the substitution of less valuable stones for more valuable. Unfortunately, the nomenclature of gems, as adopted by jewellers, rather offers an opening in this direction. Thus stones of a red colour are often known collectively as ruby with some qualifying prefix: *e.g.* 'spinel-ruby' (=spinel), 'Cape ruby' (=pyrope garnet), and 'Siberian ruby' (=tourmaline), the true ruby ('Oriental ruby' of jewellers) being, of course, corundum; or again, 'Oriental emerald' (=corundum), 'Uralian emerald' (=demantoid garnet), 'lithia-emerald' (=spodumene) and 'Brazilian emerald' (=tourmaline), the true emerald being beryl of a grass-green colour. In the same way, yellow quartz ('Spanish topaz' or 'Occidental topaz') is often mistaken for and sold as topaz. Other deceptive terms of a like nature are 'Marmorosch diamonds,' 'Cornish diamonds,' 'Bristol diamonds,' &c., for small sparkling crystals of quartz; and 'Matura diamonds' (from Matura in Ceylon) for zircon of a brilliant lustre, which has been decolorised by the application of heat. The latter, as well as colourless corundum ('white sapphire'), have occasionally been passed off as diamonds.

Other attempts have been made to produce gems of much the same chemical composition as the genuine stones. For example, green glass with the composition of emerald. Very successful imitations of turquoise have been obtained by submitting to pressure a precipitate having the same composition as the natural mineral.

The artificial colouring of natural stones is also extensively practised. Almost all cut agates have been so treated (*v.* AGATE). Chalcedony can be so cleverly coloured a delicate green with salts of nickel or chromium, as to be practically indistinguishable from the more expensive chrysoprase. A pale-coloured jasper or hornstone, quarried at Nunkirchen, near Merzig, in Rhine Province, is coloured artificially by soaking first in a solution of ferrous sulphate and afterwards in one of potassium ferrocyanide. Beads and other small ornaments of this material are cut at Oberstein and are now (1921) sold in large quantities as 'lapis-lazuli.' It is readily distinguished from true lapis-lazuli by its greater hardness and density, and by the presence of small patches of crystalline quartz, which does not take this colour. The colour of many gem-stones can be changed by heating or by exposure to the emanations of radium. A trick of the meanest kind is to smear violet ink or other bluish colouring matter on the surface of a yellowish ('off-coloured') diamond, so giving it the appearance of a colourless gem.

References.—M. Bauer, Precious Stones, English transl. by L. J. Spencer, 1904; J. Escard, Les Pierres précieuses, Paris, 1914.

L. J. S.

GENESERINE, GENESEROLINE, *v.* ORDEAL BEAN.

GENISTA TINCTORIA *v.* DYER'S BROOM.

GENISTEIN *v.* DYER'S BROOM.

GENISTEINE $C_{16}H_{28}N_2$, a homologue of sparteine, and found associated with that alkaloid in the common broom, and may be isolated from the mother liquor from the crystallisation of sparteine sulphate; m.p. 60·5°, b.p. 177°–178° (uncorr.) at 22 mm. It forms a hydrate $C_{16}H_{28}N_2,H_2O$, which melts with loss of water at 117°; $[\alpha]_D = -52{\cdot}34$ in absolute alcohol (4 p.c. sol.). Genisteine is a saturated base, not reducing permanganate in acid solution; it does not contain a methoxyl group attached to nitrogen. It is a di-acid base (mono-acid to phenol-β-phthalein), yielding a *picrate*

$$C_{16}H_{28}N_2{\cdot}2C_6H_2(OH)(NO_2)_3$$

m.p. 215° (decomp.), and a *platino-chloride* $C_{16}H_{28}N_2,2HCl,PtCl_4,2{\cdot}5H_2O$, which loses its water at 110°, and decomposes at 235° without melting (Valeur, J. Pharm. Chim. 1913, 8, 573).

GENTHITE *v.* GARNIERITE.

GENTIACAULIN, GENTIAMARIN, GENTIANOSE, GENTIIN, GENTIOBIOSE, GENTIOPICRIN, GENTISIN, *v.* GENTIAN.

GENTIAN. *Gentianæ radix,* B. P.; *Gentiana,* U.S.P. (*Racine de Gentiane,* Fr.; *Enzianwurzel,* Ger.) The dried root of the *Gentiana lutea* (Linn.) (Bentl. a. Trim. 182) is used in medicine as a bitter tonic. Its physiological activity appears to depend upon the presence of 2 p.c. of a bitter crystalline glucoside, *gentiopicrin, gentianbitter,* or *gentianin,* which was first obtained in a definite form by Kromayer (Arch. Pharm. 110, 25).

To prepare gentiopicrin, the fresh gentian root is cut into small pieces and quickly dropped into boiling alcohol in order to destroy the ferment which is present in the root and would otherwise lead to loss of glucoside. Carefully dried roots may, however, be used (Bourquelot and Bridel, J. Pharm. Chim. 1910, [vii.] 1, 156). The liquid is boiled for 30 minutes, cooled, and filtered. The alcohol is then removed by evaporation, the residual liquid mixed with calcium carbonate, filtered, evaporated to a syrup, and allowed to stand for a fortnight to crystallise. The crystals obtained are purified by recrystallisation from a mixture of equal volumes of chloroform and 95 p.c. alcohol (Bourquelot and Hérissey, Compt. rend. 131, 113). Gentiopicrin has the composition

$$C_{16}H_{20}O_9{\cdot}\tfrac{1}{2}H_2O$$

It melts at 122°, or, when anhydrous, at 191° (Tanret, *ibid.* 1905, 141, 207). By the action of dilute acids or emulsin, gentiopicrin breaks up into dextrose, and of *gentiogenin,* $C_{10}H_{10}O_4$ needles, m.p. 185°, which is soluble in alcohol, but almost insoluble in water, and not bitter (Tanret).

The mother liquors resulting from the purification of gentiopicrin contain a glucoside, *gentiin* $C_{25}H_{28}O_{14}$, which forms microscopic slightly yellow needles, m.p. 274° (decomp.). It is slowly hydrolysed by dilute sulphuric acid at 100°, forming dextrose (1 mol.), xylose (1 mol.), and *gentienin* $C_{14}H_{10}O_5$ (1 mol.).

$$C_{25}H_{28}O_{14}+2H_2O \\ =C_{14}H_{10}O_5+C_6H_{12}O_6+C_5H_{10}O_5$$

The last-named compound, on heating, begins to sublime at 195° and melts at 225°. It is isomeric with gentisin, another constituent of gentian to be described presently, but melts at a lower temperature, and gives a yellow coloration with nitric acid. Gentisin, under these circumstances, gives a green colour (Tanret, Compt. rend. 141, 263). The alcoholic extract of gentian root, from which gentiopicrin separates, also contains a third, amorphous, glucoside, *gentiamarin,* which has the composition $C_{16}H_{22}O_{10}$ or $C_{16}H_{20}O_{10}$. On hydrolysis with acids, gentiamarin yields an amorphous brown substance; with emulsin, dextrose and an amorphous maroon-coloured substance distinct from gentiogenin (Tanret, Bull. Soc. chim. 1905, [iii.] 33, 1071).

Gentian also contains, in very small proportion, another compound which, though physiologically inactive, is much better known. It is a yellow crystalline acid, *gentianic acid, gentisin,* or *gentianin* $C_{14}H_{10}O_5$, and by the earlier investigators (Gm. 16, 178) was confused with gentian-bitter or gentiopicrin, and to both these compounds the name 'gentianin' has been applied (Henry and Caventou, J. Pharm. Chim. 7, 173; Trommsdorff, Annalen, 21, 134; Leconte, *ibid.* 25, 202; Baumert, *ibid.* 62, 106; Hlasiwetz and Habermann, *ibid.* 175, 63; 180, 348).

Gentisin crystallises in large pale-yellow silky needles. Heated to 200°, it darkens in colour, and sublimes with decomposition at 300°–400°. It is nearly insoluble in water, at 16°, 1 part requiring 3630 parts of water for solution, but in alkaline solutions and in hot alcohol it dissolves readily. Melted with potash, acetic acid, phloroglucin and gentisic acid

$$C_6H_3(COOH)(OH)(OH)$$

(1 : 2 : 5) are formed (H. and H.).

Gentisin has been obtained synthetically by Kostanecki and Tambor (Monatsh. 15, 1), and is the methyl ether of gentisein, 1 : 3 : 7-trihydroxyxanthone $OH{\cdot}C_6H_3{<}\genfrac{}{}{0pt}{}{O}{CO}{>}C_6H_2(OH)_2$.

Pectin is present in gentian root in large proportion. This yields mucic acid on oxidation by dilute nitric acid and arabinose on hydrolysis with dilute sulphuric acid (Bourquelot and Hérissey, J. Pharm. Chim. [vi.] 8, 49). Fermentable sugar is present in so large a proportion that it has led to the root being employed in Switzerland and Bavaria in the manufacture of spirit (*see* below). Investigations carried out by Bourquelot and his co-workers (Bourquelot and Nardin, Compt. rend. 126, 280; Bourquelot and Hérissey, *ibid.* 131, 750; 135, 290) show that fresh gentian root contains *gentianose*, a hexotriose, $C_{18}H_{32}O_{16}$, which melts at 207°–209°, and is dextro-rotatory. It does not reduce Barreswil's (Fehling's) solution, but, if boiled with dilute sulphuric acid or acted upon by invertase, it becomes lævo-rotatory, and acquires considerable reducing power, having become hydrolysed into lævulose and a new hexobiose, *gentiobiose*, which, by more vigorous treatment, can be hydrolysed into 2 molecules of dextrose. For derivatives *v.* Hudson and Johnson, J. Amer. Chem. Soc. 1917, 39, 1272.

For the detection of gentian-bitter in beer, *v.* Dragendorff (Chem. Zentr. 1881, 285 and 299); Allen (Analyst, 12, 107; 13, 43).

Various other species of gentian contain gentiopicrin and gentianose (Bridel, J. Pharm. Chim. 1913, [vii.] 7, 289, 392, 486; 1914, [vii.] 10, 62; Compt. rend. 1912, 155, 1164; 1913, 156, 627); but *G. acaulis* roots contain no gentiapicrin but *gentiacaulin*, $C_{47}H_{60}O_{29}$, m.p. 145°–160°, $[\alpha]_D -63{\cdot}84°$ (Bridel, J. Pharm. Chim. 1913, [vii.] 8, 241; 1914, [vii.] 10, 329). For seasonal variations of constituents in *G. lutea*, *v.* Bridel (J. Pharm. Chim. 1911, [vii.] 3, 294). Gentiopicrin, 2 p.c., slightly increased in June and July; gentianose, 3–5 p.c., maximum in September; in May and June it is replaced by gentiobiose.
G. B.

GENTIAN BLUE 6 B. *Spirit Soluble Blue, Spirit Blue O, Opal Blue v.* TRIPHENYLMETHANE COLOURING MATTERS.

GENTIAN ROOT. The *Gentiana lutea* (Linn.), from which the gentian root is derived, chiefly occurs in mountainous districts, especially in Switzerland and the Tyrol. There is present in the root of this and other species of *gentiana* a bitter principle which is said to possess valuable tonic virtues, and on this account some quantity of the material is imported into this country for medicinal purposes.

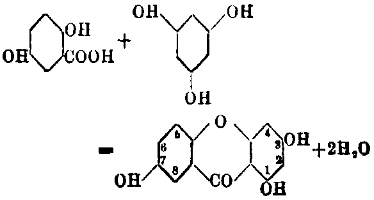
Gentisin, the colouring matter of gentian root, was first isolated by Henry and Caventou (J. Pharm. Chim. 1821, 178), and was shown by Baumert (Annalen, 62, 106) to possess the formula $C_{14}H_{10}O_5$. Hlasiwetz and Habermann (*ibid.* 175, 63; 180, 343), somewhat later, found that gentisin contains two hydroxyl groups, and when fused with potassium hydroxide, *phloroglucinol* and *gentisic acid* (hydroquinone carboxylic acid) are produced from it. By the action of hydrochloric acid on fused gentisin, methyl chloride was evolved, a probable indication of the presence of a methoxy-group. To prepare gentisin (Baumert, *l.c.*), the root is well washed with water, then extracted with alcohol, and the extract evaporated to a small bulk. The residue is washed with water to remove the bitter principle, and then with ether to extract plant wax. For purification, the crude colouring matter is repeatedly crystallised from alcohol: 10 kilos. of the root yield about 4 grams of the substance. Gentisin crystallises in yellow needles, is sparingly soluble in alcohol, and dissolved in alkaline solutions with a yellow colour.

Gentiscin $C_{13}H_8O_5,2H_2O$. When gentisin is digested with boiling hydriodic acid, it is converted into gentisein with evolution of 1 molecule of methyl iodide. Gentisein consists of straw-yellow needles, melting at 315°, and gives with sodium amalgam a blood-red coloration, whereas gentisin, by a similar method, yields a deep green-coloured liquid (**v.** Kostanecki, Monatsh. 12, 205). By the action of acetic anhydride, gentisein is converted into a *triacetyl* derivative, $C_{13}H_5O_5(C_2H_3O)_3$, needles, m.p. 226° (**v.** Kostanecki, *l.c.*); but on methylation with methyl iodide, a *dimethyl ether*

$$C_{13}H_5O_2(OH)(OCH_3)_2$$

yellow needles, m.p. 167°, is produced (**v.** Kostanecki and Schmidt, Monatsh. 12, 318).

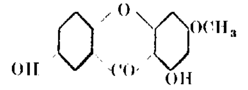
Partial methylation converts gentisein into gentisin, and it is thus certain that the latter consists of *gentisein monomethyl ether*. V. Kostanecki and Tambor (Monatsh. 15, 1) obtained gentisein by distilling a mixture of phloroglucinol and hydroquinone carboxylic acid with acetic anhydride



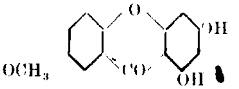
and its constitution is therefore represented as 1 : 3 : 7-trihydroxy-xanthone. By a study of *disazobenzene-gentisin*: $C_{14}H_8O_5(C_6H_5N_2)_2$, scarlet-red needles, m.p. 251°–252° (Perkin, Chem. Soc. Trans. 73, 1028), which gives the diacetyl derivative, $C_{14}H_6O_5(C_2H_3O)_2(C_6H_5N_2)_2$, orange-red

needles, m.p. 218°–220°, it has been shown that gentisin itself possesses the constitution I.

I.



II.



As gentisin yields by means of methyl iodide only a monomethyl ether, the original methoxy-group cannot be in the position (1). On the other hand, if gentisin is represented by the formula II, the azobenzene groups would enter the positions 4 and 2, and from such a compound an acetyl-derivative cannot be obtained (compare *disazobenzene phloroglucinol*)

Gentisin is a feeble dyestuff, and gives on wool mordanted with chromium, aluminium, and tin respectively, pale-green yellow, pale bright yellow, and very pale cream-coloured shades (Perkin and Hummel, Chem. Soc. Trans. 1896, 69, 1290). A. G. P.

GENTIANIC ACID *v.* GENTIAN.

GENTIANOSE *v.* CARBOHYDRATES.

GENTIIN *v.* GLUCOSIDES.

GENTIOPICRIN *v.* GENTIAN; *also* GLUCOSIDES.

GENTISIC ACID *v.* GENTIAN and PROTOCATECHUIC ACID.

GEOLYTE *v.* ZEOLITES.

GEOSOTE *v.* SYNTHETIC DRUGS.

GERANINE *v.* AZO- COLOURING MATTERS and PRIMULINE.

GERANIUM OIL *v.* OILS, ESSENTIAL.

GERMANIUM, Ge. At. wt. 72·5 (Winkler), is the *ekasilicon* predicted by Mendeléeff. It was discovered by Winkler in 1866 in *argyrodite* $GeS_2,4Ag_2S$, in which it is present to the extent of about 6–7 p.c. (Kolbeck, Centr. Min. 1908, 331). It is also present in *canfieldite, franckeite,* and *brongniardite* (Prior and Spencer, Min. Mag. 1898, 12, 5; Shroutschoff, J. Russ. Phys. Chem. Soc. 1892, 130), but its presence in *euxenite* and *samarskite* has been denied by Lincio (Centr. Min. 1904, 142). According to Buchanan (J. Ind. Eng. Chem. 1917, 9, 661), small quantities of germanium are present in Wisconsin and Missouri zinc ores and tend to become concentrated in the residues remaining in the retorts. The metal is obtained by the reduction of the dioxide with carbon at a red heat. It is a greyish-white, brittle, readily powdered lustrous metal of sp.gr. 5·469, which melts at 958°±5°, and does not volatilise at 1350°. It oxidises in air at high temperatures, combines directly with the halogens, is insoluble in hydrochloric acid, and dissolves in *aqua regia*, forming the dioxide.

Compounds.—The metal is tetravalent, and its compounds resemble those of the silicon group.

Germanium dioxide GeO_2 is obtained from argyrodite by treatment with nitre and potassium carbonate at a red heat, then with acid, after which it is purified by being converted into the sulphide, which is roasted and treated with nitric acid. The oxide forms a white powder having acid properties, but soluble in acids, and is readily reduced by carbon, sodium or magnesium. A colloidal solution of germanium hydroxide is obtained by decomposing an alkaline solution of the dioxide with carbon dioxide.

Germanous oxide GeO is a greyish-black powder, and the corresponding hydroxide $Ge(OH)_2$ is a yellow powder obtained by the action of alkalis on germanium chloroform or chloride. According to Hantzsch (Zeitsch. anorg. Chem. 1902, 30, 289), in aqueous solution it is a weak monobasic acid, and has the constitution HGeO·OH, being analogous to formic acid.

Germanium chloroform $GeHCl_3$ is obtained when germanium is heated in a current of hydrogen chloride, a colourless liquid being thus formed, which separates into two layers, of which the heavier is germanium chloroform; it is a colourless fuming liquid, b.p. 75°. The lighter liquid is *germanium oxychloride* $GeOCl_2$; it is similar in properties to the chloroform, but is less mobile, and boils above 100°. *Germanium dichloride* $GeCl_2$, the *tetrachloride* $GeCl_4$, and the corresponding tetrabromide, -iodide, and ethide $GeEt_4$, are also known.

Germanium tetrafluoride $GeF_4,3H_2O$ combines with hydrofluoric acid, forming *germanofluoric acid*, of which the *potassium* salt K_2GeF_6 forms hexagonal crystals isomorphous with those of ammonium silicofluoride.

Germanium disulphide GeS_2 is the most characteristic of the germanium derivatives, and is prepared by passing sulphuretted hydrogen in a solution of germanium dioxide; it is a white powder, soluble in water to some extent and in ammonium sulphide (Vogelen, Zeitsch. anorg. Chem. 1902, 30, 329). The monosulphide GeS and thiogermanates are also known (J. pr. Chem. 1887, [2] 36, 177; Ber. 1888, 21, 131).

Germanium hydride GeH_4 is formed when germanium chloride is reduced with sodium amalgam. It is also formed as a mirror in the Marsh apparatus, as in the arsenic test. The mirror is red by transmitted and green by reflected light, is soluble in sodium hypochlorite, but with difficulty in hot hydrochloric acid. With sulphuretted hydrogen it forms the sulphide; heated in air it gives the dioxide, whilst with silver nitrate it forms a black silver germanium compound, probably $GeAg_4$ (Vogelen, *l.c.* 325).

GERMAN SILVER *v.* NICKEL.

GERMOL. A disinfectant consisting of crude cresols.

GERSDORFFITE. Sulph-arsenide of nickel, NiAsS, crystallised in the cubic system. The nickel (35·4 p.c. according to the formula) is usually partly replaced isomorphously by iron, and less often by cobalt. Analyses show Ni 16·24–35·97 p.c., with Fe nil–16·64 and Co nil–14·12 p.c. Crystals are usually octahedral in habit, and they show good cleavages parallel to the faces of the cube. The colour is steel-grey with metallic lustre, but usually the material is tarnished and dull black; the streak is greyish-black. Sp.gr. 5·6–6·2; H. 5. The mineral occurs in metalliferous veins, and has been recorded from several localities in Central Europe; also from Loch Fyne in Scotland, Sudbury in Ontario, &c. L. J. S.

GESILIT *v.* EXPLOSIVES.

GETAH WAX *v.* Waxes.

GETALIN, GITONIN, *v.* Digitalis.

GEYSERITE or **SILICEOUS SINTER.** (Ger. *Kieselsinter.*) An opaline form of hydrated silica deposited by the hot springs (geysers) of volcanic regions. It is white or greyish in colour and porous in texture. On the exterior it usually assumes fantastic shapes—stalactitic, filiform, and cauliflower-like masses—and it is sometimes found encrusting plants. Compact-massive and pulverulent forms also occur. Sp.gr. 1·8–2·0. The material consists of nearly pure silica, SiO_2 82–97 p.c. with H_2O 3–10 p.c., and small amounts of aluminium, iron, calcium, magnesium, and alkalis. Immense deposits occur in Iceland, New Zealand, Luzon in the Philippine Islands, Azores, and Yellowstone National Park in Wyoming. Its use has been suggested for the manufacture of porcelain, glass, silica-glass, &c., and as an inert filling material. L. J. S.

GHATTI *v.* Gums.

GHEDDA or **EAST INDIAN WAX.** Differs from ordinary beeswax in containing only one alcohol, ceryl alcohol, present in the form of esters. M.p. 62°–63°, solidifies at 59°–58°, acid value 5–7·5, ester value 86–92.

The wax contains approximately 48 p.c. of ceryl alcohol, 5 p.c. of heptacosane, $C_{27}H_{56}$, 2 p.c. of hentriacontane, $C_{31}H_{64}$, 24–25 p.c. of hydroxymargaric acid, $C_{17}H_{34}O_3$, m.p. 55°–56°, 1·5–2 p.c. of an isomeric hydroxymargaric acid, m.p. 71°–72°, 9–10 p.c. of margaric acid, 8–9 p.c. of palmitic acid, 2 p.c. of "Ghedda" acid, and 1 p.c. of cerotic acid, with traces of formic, acetic and butyric acids and tarry matter.

"Ghedda" acid ($C_{34}H_{68}O_2$?), m.p. 94·5°–95°, forms mossy aggregates of white needles; sparingly soluble in ether. (Lipp and collaborators, J. pr. Chem., 1912, [ii.] 86, 184; *idem.* 1919, [ii.] 99, 243, 99, 256.)

GHEE. A clarified butter used in the East mainly for cooking.

GIALLOLINO or **NAPLES YELLOW** *v.* Pigments.

GIANT POWDER *v.* Explosives.

GIBBSITE or **HYDRARGILLITE.** Hydrated alumina, $Al_2O_3{\cdot}3H_2O$ (Al_2O_3 65·4 p.c.), crystallised in the monoclinic system. It usually forms white or greyish, stalactitic or mamillated, encrusting masses. Crystals, to which the name hydrargillite is more particularly applied, have the form of thin six-sided plates with a pearly lustre on the perfect basal cleavage; these are found in a magnetite-bearing schist at Shishimsk, near Zlatoust in the Urals, and in nepheline-syenite in the Langesund-fjord, Norway. Sp.gr. 2·3–2·4; H. 2½–3½. A bed, about a foot in thickness, of nodular plates of amorphous material is found beneath the soil overlying igneous rocks over a wide area in the Palni Hills in Madras. As a constituent of bauxite and laterite it is of wide distribution, and it has also been identified in some highly aluminous fire-clays. If found in sufficient quantity it would be of value as an aluminium ore.

L. J. S.

GILO, GOLANCHA, and **GULOH.** Indian names for *Tinospora cordifolia* (Miers). This plant flourishes in India, the drug being sold extensively in the bazaars as a tonic and antiperiodic, in the form of cylindrical pieces, 2 to 5 cm. long and 1 to 5 cm. in diameter. It is a perennial creeper, climbing to the summit of the highest trees, its branches putting forth roots which, reaching to the ground, initiate a fresh growth. Roots, stem, and leaves are equally in demand as a drug. The Indian pharmacopœia commends its use as a tincture (4 to 8 c.c. *in die*); as an extract (0·6 gram to 1 gram *per diem* in the form of pills); and as an infusion (1 : 10), of which 60 c.c. to 90 c.c. are to be taken thrice a day. The stems contain verberin, an uncrystallisable bitter substance, changed by dilute sulphuric acid into a glucoside, and a bitter kind of starch meal known as 'palo' (J. Soc. Chem. Ind. 6, 49).

GILSONITE. A mineral hydrocarbon occurring in Utah, the Philippines, and elsewhere, used in the paving industry, and in the manufacture of electrical insulators, roofing materials, for waterproofing pipes and aqueducts, preventing corrosion of iron plates of ship's bottoms, coating wire fencing, sea-walls, poles, &c., lining tanks for chemicals, paints, lubricants for heavy machinery, rubber substitute, binder for briquettes, &c.

GIN or **GENEVA** is a spirituous liquor made from spirit derived from grain and distilled with juniper berries and other flavouring substances. The term is a corruption of the word '*genièvre*' or '*junever*,' the French and Dutch equivalents respectively for *juniper*, which is the essential flavouring ingredient.

The principal varieties are the English, known as 'gin,' and the Dutch, described as 'Geneva,' 'Hollands,' and 'Schnapps.' The difference between them is chiefly one of flavour, and each manufacturer has his own special recipe, which is carefully preserved as a trade secret. The principal flavouring ingredients used besides juniper are angelica root, almond cake, calamus root, cardamom seeds, cassia buds, coriander seeds, creosote, liquorice powder, orris root, sweet fennel, and turpentine.

The grain used is almost invariably a mixture of maize, malt, and rye, the proportions being usually about 75 p.c. maize, 15 p.c. malt, and 10 p.c. rye for English gin, and about equal parts of each for the Dutch varieties, although sometimes maize is absent.

During the Napoleonic wars at the beginning of the last century, the use of corn, owing to its scarcity, was prohibited in the United Kingdom for the manufacture of spirit, and the manufacturers had recourse to molasses or low-grade sugar. This, however, produces a very inferior quality of gin, which is essentially a grain spirit, but it is still made, chiefly for exportation, by the addition of juniper oil or similar flavouring agent to the crude spirit.

In England, patent-still spirit is generally employed as a basis, but it is preferably not rectified so highly as to deprive it of the characteristic flavour of grain spirit. The flavouring ingredients are in some cases added directly or they are separately distilled and the distillate added to the spirit to be flavoured. Another and probably the best method is to redistil the spirit, after the addition of the flavouring ingredients, in a kind of pot-still with a long head or other simple rectifying arrangement.

In Holland, the manufacture is carried on mainly at Schiedam, where pot-stills [illegible] chiefly employed. The spirit is subjected to three or four rectifications, when it is known as 'moutwijn' or 'maltwine.' This is sold to the manufacturers of Geneva or Hollands who flavour it by methods similar to those above described for English gin.

The best '*Hollands*' is said to be prepared as follows: A mixture of two measures of ground rye with one measure of ground barley malt is mashed with about 24 gallons of water for each cwt. of the mixed meal. The mashing being completed, the sp.gr. of the wort is reduced by cold water to between 1033 and 1038. It is then fermented, after which the whole is thrown into a still. To the first product of distillation, called *low wines*, a varying proportion of juniper berries with a little salt is added, and it is redistilled. The spirit which now passes over is flavoured with essential oils or resins derived from the juniper as well as from the rye and barley used in brewing.

Sweetened gin (*e.g.* 'Old Tom' and 'Old Geneva') is made by the addition of sugar syrup to plain gin. The syrup is prepared by dissolving refined sugar in its own weight of pure water. Sometimes it is flavoured with orange-flower water, and is known as 'capillaire.' The clear solution is added in the proportion of about 6 gallons of syrup to 100 gallons of gin.

Plymouth gin is a special variety of gin made in Plymouth, and used extensively in the West of England. It has a characteristic flavour, said to be due to ether resulting from the addition of a little sulphuric acid to the spirit to be rectified.

The adulteration of gin, except by dilution with water, is not common. Alkaline carbonates, and sometimes alum and salts of zinc and lead, have been found. Juniper wood oil and turpentine oil are occasionally used as substitutes for or admixed with the oil from the juniper berry.

By the Sale of Food and Drugs Amendment Act, 42 & 43 Vict. c. 30, s. 6, gin may not be sold at a strength below 35 under proof, unless declared to be diluted. The percentage of water added may be found by multiplying the excess of degrees under proof beyond 35 by the factor 1·54. For example, a gin of strength 45 u.p. contains 10×1·54, or 15·4 p.c. of added water over and above that present in gin at the minimum statutory strength of 35 u.p.

J. C.

GINGELLY or **GINGILI OIL** *v* SESAMÉ OIL.

GINGER.

Description.—Ginger is the dried rhizome, either whole or ground to a powder, of *Zingiber officinale* (Roscoe), a plant 3 to 4 feet in height, which grows wild in India and China and is cultivated extensively in most tropical countries. At the present time, the chief kinds which find their way into the English market are Jamaica, Calicut, Cochin, African, Japanese, and in less quantity, Bombay. Japanese ginger is not derived from *Z. officinalis* and is therefore not *official* for medicinal purposes.

Preparation and properties.—The rhizomes are dug up when the plant is about a year old, washed, and dried in the sun. In some cases the epidermis is removed by scraping or cutting, in others the root is dried intact.

To meet the popular prejudice in favour of a white product various methods of treating the root are adopted. The commonest consists in immersion in milk of lime, when the coating of lime left after drying is of advantage in preventing the attacks of insects, fungi, &c. Gypsum and chalk are also used with a similar object. Ginger is also said to be bleached with sulphurous acid or bleaching powder, but most of the so-called bleached ginger has probably only been 'limed.'

The unscraped root has a yellow-brown wrinkled surface, while the scraped variety is smooth and nearly white. The pieces are, as a rule, from 2 to 4 inches in length, knotted and bent, flattened in section and with a short fracture.

On being cut with a knife, the best ginger presents a soft floury surface, inferior qualities appear hard, resinous, and shiny.

The chief structures observed when ground ginger is examined under the microscope are the starch grains, the vessels, reticulated, spiral, and scalariform, the sclerenchymatous cells, broad bast fibres with somewhat thin walls and occasionally thin-walled polygonal parenchymatous cells and oleoresin cells, which have escaped destruction during the grinding. The starch grains are, for the most part, elongated, simple (except in Japan ginger where aggregates of small granules occur), sack-shaped or oval, and vary in length from 12 to 50μ, the majority being between 20 and 30μ. The hilum is placed close to the narrow end and the striations are visible in the larger granules if properly illuminated.

Ginger is used as a condiment and flavouring agent and in medicine as an aromatic stimulant and carminative.

Composition.—Its chief characteristic constituents are a volatile oil to which the aroma is due; a fixed oil, gingerol, which gives the pungent flavour; starch and resin. The following figures (Richardson, from Leach, Food Inspection and Analysis, 446) will afford some idea of its composition:—

TABLE I.

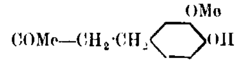
—	Water	Ash	Volatile oil	Fixed oil and resin	Starch	Crude fibre	Albuminoids	Undetermined	Nitrogen
Calcutta	9·60	7·02	2·27	4·58	49·3	7·45	6·30	13·4	1·01
Cochin	9·41	3·39	1·84	4·07	53·3	2·05	7·00	18·9	1·12
Unbleached Jamaica . .	10·49	3·44	2·03	2·29	50·6	4·74	10·85	15·6	1·74
Bleached Jamaica (London) .	11·00	4·54	1·89	3·04	49·3	1·70	9·28	19·2	1·48
,, ,, (America) .	10·11	5·58	2·54	2·69	50·7	7·65	9·10	11·7	1·46

Determinations by Garnet and Grier (Pharm. J. 1909, 83, 159–160) give the gingerol as from 1·1 to 2·2 p.c.

The composition of gingerol has been further investigated by Lapworth, Pearson, and Royle (Chem. Soc. Trans. 1907, 111, 777), who found the pungent principle of ginger to be a mixture of saturated phenolic compounds derived from a residue of zingerone (*v.* below) in association with a molecular proportion of the residue of a saturated aliphatic aldehyde. The gingerol was obtained by extracting the residue from an alcoholic extract of ginger with 35 p.c. alcohol, evaporating *in vacuo* at minimum temperature, removing water as far as possible and re-extracting with 50 p.c. alcohol. To the solution milk of lime was then added, and after standing the clear liquid was neutralised with hydrochloric acid, and the alcohol again removed under reduced pressure. The resulting oil was separated from water, dissolved in chloroform, the solution dried and evaporated. After fractional extraction with hot petroleum and removing the latter, a viscous yellow oil was obtained which was further purified by distillation in a cathode ray vacuum. The best samples of the faintly yellow oil probably contained about 25 p.c. of impurities.

From it was prepared methyl-gingerol, which crystallises in slender needles, m.p. 64°C., optically active in 2 p.c. chloroform, $\alpha_{D}^{21} = 27·3°$.

Zingerone. Nomura (Chem. Soc. Trans. 1917, 111, 769) has prepared from ginger, also Lapworth and Dykes from gingerol (*ibid.* 783), a ketonic body, *Zingerone*, the yield amounting to about 0·04 p.c. of the ginger, to which they agree in assigning the formula $C_{11}H_{14}O_3$, the constitution of the metone being



$$\mathrm{COMe{-}CH_2{\cdot}CH_2}\overset{\mathrm{OMe}}{\bigcirc}\mathrm{OH}$$

From ginger it was prepared by shaking the ethereal extract, previously evaporated to a syrup, with 2 p.c. sodium hydroxide, passing carbon dioxide through the alkaline liquid and extracting with ether.

The ethereal solution, washed first with 2N.-sodium carbonate and then with water, until no longer alkaline, was evaporated, distilled under a pressure of 13–23 mm. and afterwards under 0·5 to 1 mm. until the temperature of the water-bath reached 320°. From the distillate the bisulphite compound of the ketone was prepared. This was washed with ether, decomposed with sodium carbonate, and the resulting oil extracted with ether, the solution washed with water, dried over anhydrous sodium sulphate, and evaporated.

The oil, when shaken with a crystal of the solid ketone, solidified, and was recrystallised from light petroleum. It forms colourless needles, rhombohedra, or lustrous plates, m.p. 40°–41° (Nomura), 31°–34° (Lapworth, Pearson, and Royle), and has the odour of salicylaldehyde, and the pungent taste of ginger. It dissolves easily in most organic solvents, except light petroleum, but sparingly in water, and is only slightly volatile in steam. Warmed with concentrated mineral acids the mixture shows a striking series of colour changing from faint yellow to brown, and then deep purple; on adding alkali it becomes blue, green, and finally colourless. The mixture gives a red colour with Millon's reagent, dissolves to a green solution with alcoholic ferric chloride, and reduces ammoniacal silver nitrate.

From it were prepared a *monobenzoyl* derivative, colourless crystals, melting at 126°–127°; a crystalline *monoacetyl* derivative, m.p. 40°–42°; also *Methyl Zingerone*, m.p. 55°–56°; *Methyl Zingerone-oxime*, m.p. 93°–93·5°; and *Ethyl Zingerone*, m.p. 66°.

In addition to zingerone, Nomura finds in Japanese ginger a pungent principle *Shogaol*, $C_{17}H_{24}O_3$, b.p. 231°–238°/15·5 mm.; sp.gr. 1·0448/25°, containing a methoxyl radicle and a hydroxyl and ketonic group. Nomura and Nozawa have sought to establish to what constitutional factors the pungency of the principles in ginger is due (J. Soc. Chem. Ind. 1918, 606, A.).

Brooks and Humphrey (J. Amer. Chem. Soc. 1916, [38] 430) prepared from ginger oil freed from terpenes and sesqui-terpenes a tertiary alcohol distilling between 154° and 157° at 14·5 mm. pressure, having the formula $C_{15}H_{26}O$, which possessed the peculiarly fragrant odour of ginger. From it the hydrocarbon in zingiberine $C_{15}H_{24}$, boiling from between 254° to 257°, was obtained.

Adulteration.—The only form of adulteration to which whole ginger is subject is the addition of or substitution by ginger from which more or less of the strength has been removed by extraction with dilute alcohol or water, in the manufacture of ginger beer, &c.; or with strong alcohol for the preparation of the essence or tincture. Ground ginger may be adulterated by the addition of foreign starches—wheat, maize, rice, turmeric; and in the past at all events, cayenne pepper and turmeric have been employed to restore the pungency and colour where these have been reduced by the practices already referred to.

Mineral matter, especially calcium carbonate and calcium sulphate, may also be present in excess, owing either to their deliberate addition or to the too liberal employment in the preparation of the article.

Detection of adulteration.—The detection of exhausted ginger in small proportion is at present impossible, and even when the amount is substantial, the problem is by no means an easy one, because the constituents which are removed by extraction with alcohol and water occur in widely varying proportions, even in different samples of the same kind of ginger, while, in the case of different kinds, the variations are still more marked. The tables on p. 377 show this and also the changes in composition brought about by the processes of extraction as commercially carried out.

The most useful determinations for the detection and estimation of exhausted ginger are the ash soluble in water, the alcoholic extract after extraction with ether, and the cold water extract, and these may with advantage be supplemented by the light petroleum extract or the methyl alcohol extract and a determination of the potash. Microscopical examination is of no assistance but the taste and smell of the sample are of limited utility on account of the

TABLE II.—RESULTS OF ANALYSIS OF 87 SAMPLES OF GINGER.
(Zeit. f. Untersuch. des Nahrungs u. Genuss. 1907, 14, 549.)

——	Water	Total ash	Soluble ash	Sand	Ether extract (volatile)	Ether extract (fixed)	Alcohol extract after ether	Light petroleum	Methyl alcohol extract
Highest . . .	13·85	9·33	4·51	3·79	3·08	8·08	4·46	5·77	9·58
Lowest . . .	9·20	3·24	1·52	0·05	0·90	2·84	1·12	1·95	3·82
Extracted Cochin . .	13·26	3·28	0·99	0·11	0·48	1·32	0·67	0·69	1·54
,, Bengal . .	13·42	4·52	1·93	0·97	0·46	1·18	0·55	0·54	1·90

TABLE III.
(Clayton, Analyst, 24, (1899) 123.)

——	No. of samp.	——	Water	Cold water extract	Ether extract	Alcohol 100 p.c. extract after ether	Light petroleum extract (fixed)	Ash	Soluble ash	Ash of cold water extract	Alkalinity of soluble ash (as K_2O)
Whole ginger .	11	max.	14·76	15·88	3·71	1·81	2·00	6·19	3·81	4·52	—
		min.	11·18	6·69	6·88	0·88	1·24	2·67	1·27	1·74	—
		mean	13·33	9·96	4·88	1·37	1·60	3·71	2·27	3·10	—
Ground ginger (commercial) .	9	max.	11·83	15·40	9·37	1·21	3·57	6·47	3·48	3·84	0·33
		min.	10·39	4·54	4·42	0·41	1·43	2·05	1·43	1·72	0·13
		mean	11·32	10·36	6·18	0·81	2·11	4·50	2·46	2·96	0·24
Exhausted ginger	10	max.	12·07	14·06	4·33	1·07	1·49	2·70	1·13	1·90	0·15
		min.	11·05	2·57	1·79	0·69	0·10	1·41	0·43	0·61	0·04
		mean	11·62	7·89	3·20	0·77	0·76	2·06	0·49	1·08	0·09

great variations in strength of the different kinds of ginger.

No legitimate manufacturing operation affects the analytical results sufficiently to cause any trouble (Clayton, *l.c.*), but it must be borne in mind that the method by which the sample has been extracted, of which the analyst is usually ignorant, considerably affects the analytical results. (For the effect of exhaustion with alcohol of different strengths, *see* Liversedge, Pharm. J. 1896, ii. 112, and for information as to methods of extraction actually employed by ginger beer manufacturers, &c., *see* Analyst, 1893, 8, 200.)

The starchy substances likely to be added to ginger may be detected by the microscope. The unsymmetrical cross observed when ginger starch is viewed under polarised light distinguishes it at once from wheat.

Capsicum may be detected by the test suggested by Garnett and Grier (Pharm. J. 1909, 441), based on the fact that the pungent flavour of gingerol is destroyed by heating with alkalis whereas that of capsicum is not.

Standards.—The United States Department of Agriculture has fixed the following standard for ginger: the starch (by diastase method) shall not be less than 42 p.c., the crude fibre not over 8 p.c., the total ash not over 8 p.c., the lime not over 1 p.c., and the ash insoluble in HCl not over 3 p.c. *British Pharmacopœia*: Alcoholic extract (90 p.c. alcohol) not less than 5 p.c., and cold water extract not less than 8·5 p.c., ash not to exceed 6 p.c., insoluble ash under 1·5 p.c. The Pharmaceutical Codex provides that the volatile oil shall be between 1 and 3 p.c., the ash between 3 and 5 p.c., and the aqueous extract not under 10 p.c.

C. H. C.

GINGER GRASS OIL *v.* OILS, ESSENTIAL.

GINGER, OIL OF, *v.* OILS, ESSENTIAL.

GINGKOIC ACID $C_{22}H_{47}$·COOH, m.p. 35°, is obtained from the fruit of *Gingko biloba* (Linn.) (Schwarzenbach, J. 1857, 529).

GIROFLE. *Dimethylphenoxylosafranine* (*v.* AZINES).

GLASERITE Aphthitalite (*q.v.*).

GLASS. History. Despite Pliny's pretty story of the accidental discovery by the Phœnicians of the mode of making glass, all evidence points to Egypt as having been the home of the art. Flinders Petrie in Arts and Crafts of Ancient Egypt, says that glassmaking, apart from pottery, does not go back further than 1600 B.C. and that blown glass was not developed until many centuries later, the glass object being fashioned round a core of sand. The Phœnicians most probably acquired the art from the Egyptians, and they carried their glassware, beads, and vases, as well as Egyptian glassware, into many countries bordering upon the Mediterranean. In the 1st century B.C. the Roman market for Egyptian glassware developed at a rapid rate, resulting in the attraction of a number of Egyptian workmen to Rome and the setting up there during the last half-century B.C. of a number of factories. Glassmaking under the Romans reached a very high standard, and in respect of some productions their manipulative skill has scarcely been surpassed. Many new shades of colour in glass were developed whilst glass engraving and the production of cameos were well advanced.

The Venetian glassmaking period dates back to the beginning of the 13th century, and reached its culminating period in the 16th and 17th centuries. The fame which the art brought to the Republic of Venice was marked by the privileged position accorded by the State to the Corporation of Glassmakers, as instanced by the enactment which permitted nobles without loss of rank to marry daughters of glassmakers, and by other laws which inflicted heavy penalties on Venetians who went abroad and taught the art of glassmaking. Elegance of form characterised the Venetian productions which were made of a lime glass, either plain or ornamented by a variety of methods including filigree work, lattice pattern and gilding.

Glassmaking was undoubtedly carried on in England, France, and Germany under Roman occupation. In later times, the earliest reference to the existence of glass manufacture in this country was in 1439 when the Countess of Warwick stipulated that no English glass should be used in the windows of the Beauchamp Chapel at Warwick. Elizabeth endeavoured to build up a native industry, but it was not until the later half of the 17th century—and especially during the 18th—that it acquired importance. London was the chief centre in the development, whilst Newcastle probably followed in order. The chief contribution of England to the glass industry was the discovery in the 17th century of lead glass, and the brilliant effect produced by the decoration of this glass by the cutting process contributed to the decline in the demand for the Venetian wares.

The intensive scientific study of glass was the outstanding feature of Germany's efforts in the last quarter of the 19th century. Already in England in 1834, Rev. V. Harcourt began a long series of investigations of the relation between the physical properties and the composition of glass, and showed that borate and phosphate glasses had valuable optical properties. This work was pursued, in later years in conjunction with Stokes, until 1864, when Harcourt died. Schott's experiments, beginning with the lithium glasses, described in 1879, were more successful in that they culminated in commercial manufacture. Early on associated with the physicist Abbe, considerable improvement was soon effected in optical glass, and, uniting with the firm of Zeiss, the first works at Jena were founded in 1884. Many new varieties of optical glass were made, whilst the information obtained in this field not only by Schott, but also by Winkelmann, Weber, and others attached to the Jena school of workers, led to great improvement in chemical glassware, thermometer glasses, and heat-resisting glass.

No glassmaking of any real note took place in America before 1800. The last twenty-five years there have been noteworthy for remarkable mechanical inventions for the manipulation of glass. In this field the Americans stand supreme.

As the result of the war, glassmaking has developed in a number of new centres. In both Great Britain and America chemical glassware superior to the best German has been produced, whilst remarkable progress has been made in England in optical glass of high quality. Japan has undertaken extensive glass manufactures, whilst India is cultivating the industry. Glassmaking is likewise being encouraged as new, or comparatively new, industries in Australia, South Africa, Brazil, and the Argentine.

GLASS.

Definition. Owing to its complexity and to the large number of possible varieties, glass cannot be brought adequately within the scope of a single or simple definition. It may be defined as an amorphous, hard, brittle substance, usually transparent, but sometimes translucent or even opaque, breaking with a conchoidal fracture and consisting of a material obtained by the fusion of one or more of the oxides, silica, boric oxide, phosphoric oxide, and the metallic oxides, followed by sufficiently rapid cooling of the fused mass as to prevent crystallisation of the components. The glass may be colourless or may be coloured either by one or more of the constituent oxides or from the effect of neutral bodies such as carbon, sulphur, and selenium. According to the definition, glass, being amorphous, will be isotropic. There are some substances, however, which, in certain optical instruments, serve as glasses but are anisotropic in character, and have properties differing in the directions of their crystallographic axes. Such crystalline substances in common use are quartz, fluorspar, and calcspar, or Iceland spar.

Properties of Glass. From their mode of preparation, ordinary glasses must be considered as mixtures of compounds, usually of silicates, but also of borates and, in rarer cases, of phosphates and arsenates. A study of the freezing point curves or equilibrium diagrams of binary and ternary mixtures of silica with other basic oxides has been the most fruitful source hitherto of our knowledge of these compounds probably present in silicate glasses (*see*, for example, Hilpert and Weilter, Ber. 1909, 42, 2969; 1910, 43, 2565. Day and Shepherd, Amer. J. Soc. 1906, 22, 265, Rankin and Wright, *ibid.* 1916, 39, 1. Shepherd and Rankin, *ibid.* 1909, 28, 301; 1915, 39, 9. Rankin and Wright, *ibid.* 1915, 39, 68); whilst the investigations of Wallace (Trans. Cer. Soc., 1909–10, 9, 172) and others have shown that some of these silicates, such as sodium and barium metasilicates, lithium and sodium metasilicates, and sodium aluminium trisilicate and calcium aluminium trisilicate (albite and anorthite) form continuous series of solid solutions; and certain others, such as lithium and calcium metasilicates, are soluble only to a limited extent in the solid state.

On rapid cooling, the viscosity of the mass increases greatly and the mixture at length sets, not at any definite temperature, but over an interval which it is not easy to define with precision. On reheating, it also softens gradually, and has no melting-point. Accordingly, the commonly prevailing view is that glass is to be regarded as a super-cooled liquid of extremely high viscosity. It is the high viscosity which is the most important factor in preventing the separation out in the crystalline form of the compounds present, although it has been suggested that even in apparently transparent glasses, incipient crystallisation may exist, thus explaining, for example, the phosphorescence of fused zinc silicate and bringing glass into line with the behaviour of certain other amorphous substances, such as sulphur, which tend to revert to the stable crystalline state (*see* Jackson, J. Roy. Soc. Arts, 1919; S. C. Bradford, J. Soc. Glass Tech. 1919, 3, 282).

The general statement made above in regard to the setting and the softening of glass, is not intended to imply that these processes are absolutely continuous. Tool and Valasek (Bureau of Standards Papers, 1920, No. 358), indeed, have shown that there is distinct discontinuity in the heating curve of a glass when softening begins, due to slight heat absorption, and a corresponding heat evolution on cooling.

Although ordinary glasses consist of mixtures of compounds, the properties of glasses can, with a considerable degree of success, be referred to the influence of the constituent oxides or added substances; indeed, in some properties there appears to be an additive relationship, as in the case of the density and the coefficient of expansion of sodium-calcium silicate glasses of similar molecular type. The following important properties are largely discussed on the basis of the effect of the constituent oxides.

Durability. Resistance to disintegrating agents such as water, aqueous solutions of salts, acids, or alkalis, atmospheric moisture and dust must be possessed by a glass if it is to be capable of service. Borate glasses and phosphate glasses, whilst possessing valuable optical properties, have hitherto been little used owing to instability in the presence of weathering agents.

Methods of testing the durability of a glass are numerous (Cauwood, English, and Turner, J. Soc. Glass Tech. 1917, 1, 153). Mylius employed a test in which iodoeosin was precipitated from an alcohol-ether solution by the alkali set free from the glass surface to which it was applied. The amount of iodoeosin precipitated per unit area of a fractured glass surface after the latter had been exposed initially to an enclosed damp space for seven days before being dipped in the iodoeosin solution for one minute at 18°C. was called the weathering alkalinity. According to the weathering alkalinity, the durability of the glasses examined was classified as h_1, h_2, h_3, h_4, h_5. Thus:

		m.gm. iodoeosin per sq metre			
Class	Types of glass	Weathering alkalinity	Durability *	Alkalinity by solution from hollow ware at 18°	at 80° *
1	Water resistant .	0– 5	h_1	0– 5	0– 20
2	Resistant glasses .	5–10	h_2	5– 16	20– 61
3	Hard apparatus .	10–20	h_3	16– 49	61–202
4	Soft " .	20–40	h_4	49–202	202–809
5	Unsatisfactory glasses	>40	h_5	>202	>809

Peddle (J. Soc. Tech. 1920, 4, 39) found that the amount of alkali extracted from powdered glass (160 mesh) by treatment with water at 80° for 1 hour was a ready measure of durability. With five optical glasses previously classified by Schott as h_1, h_2, h_3, h_4, h_5 respectively, he found:

Type of glass	Schott No.	Schott classification	m.gm. H_2SO_4 required to neutralise alkali from 100 grs. glass
Light barium flint	0463	h_1	159
Borosilicate crown	0144	h_2	362
Silicate crown .	0337	h_3	580
" " .	0203	h_4	729
" " .	0381	h_5	899

The reagents tending to corrode chemical glassware may be (1) water or salt solutions, (2) acids or acid solutions, (3) alkalis or alkaline solutions. Usually the corrosive action of alkaline solutions, such as sodium or potassium hydroxides and carbonates, is much more severe than that of acids or water. Concentrated acids, sulphuric and nitric, appear to act on lime-soda glassware to a less extent than pure water. A flask of first-class chemical glassware should not lose more than about 1 m.gm. per 100 sq. cm. when pure water is placed in a 500 c.c. flask and evaporated from 300 c.c. to 100 c.c. in two hours; hydrochloric acid solution of 20·24 p.c. strength should not extract more than 3·4 m.gm. per 100 sq. cm. when evaporated from 250 c.c. to 100 c.c. in 1½ hours in a 500 c.c. flask; 2N.-caustic soda should not extract at 100° for three hours more than about 100 mg., and 2N.-sodium carbonate not more than 35 mg. per 100 sq. cm. (Cauwood, English, and Turner, *l.c.*).

In the case of water, the amount of corrosion may more accurately be determined by the extraction of alkali; for the nature of the action, namely, first absorption of the water, followed by hydration, is such, that the net loss in weight of the glass may be less than the actual extent of corrosion. With HCl, the corrosion may be determined by evaporation of the acid extract in platinum, gentle ignition to avoid loss of the alkaline chlorides, and calculation of the weight of residue in terms of Na_2O or K_2O.

Oxides which bestow (1) resistance to water are SiO_2, B_2O_3, Al_2O_3, ZnO, PbO; (2) resistance to acids, SiO_2, Al_2O_3, CaO, B_2O_3, ZnO; (3) resistance to alkali, Al_2O_3. Acidic oxides naturally do not offer great resistance to alkaline solutions.

The weathering of optical glass has also been measured by exposing it to moist air for definite periods and also to dust. The latter may be organic and serve to condense moisture or to produce acid matter. Blobs or hair-like markings, or both, may in consequence be developed. The weathering power of optical glass can be determined most speedily by the determination of its chemical resistance to water (*see* W. E. S. Turner and collaborators, J. Soc. Glass Tech. 1917, 1, 145, 153, 213; 1918, 2, 219, 235; 1919, 3, 129, 228; E. Zschimmer, Chem. Zeit. 1901, 25, 780. C. J. Peddle, J. Soc. Glass Tech. 1920, 4, 39).

Thermal expansion appears to be a linear function of the composition in a simple series of glasses (English and Turner, J. Soc. Glass Tech. 1919, 3, 238; 1920, 4, 115; 1921, 5, 183).

In the tri-silicate series of glasses $3SiO_2xCaO$ (or MgO) yNa_2O where $x+y=1$, the calcium glasses have linear expansion ranging from $115{\cdot}3\times10^{-7}$ when CaO is 0·0 p.c. to $76{\cdot}9\times10^{-7}$ for CaO 11·63 p.c. For MgO 1·10 p.c. it is $111{\cdot}1\times10^{-7}$, and for 9·30 p.c. $59{\cdot}4\times10^{-7}$.

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* Seven days' treatment at 18°, three hours at 80°.

Glasses of comparatively small expansibility can therefore be obtained by suitably modifying the composition. Pyrex glass has a linear coefficient of 32×10^{-7}; Jena 59^{III} of 42×10^{-7}; Jena 16^{III} of $76·9 \times 10^{-7}$. Glasses rich in alkali have high expansibility. SiO_2, B_2O_3, MgO, and ZnO reduce the expansibility.

Winkelmann and Schott found empirically that the cubical expansion ($3a$) of a glass could be represented by the formula $3a = xa + yb + zc$ where x, y, and z are the percentages of each oxide and a, b, and c the contribution to the total cubical expansion which each 1 p.c. of the oxide makes.

The factors a, b, c, &c. calculated by Winkelmann and Schott have been shown by English and Turner not to be correct in some cases. The recalculated values of $3a$ for four oxides are SiO_2, 0·15; CaO, 4·9; Na_2O, 13·0; and MgO, 1·35, multiplied by 10^{-7} in each case.

The rate of expansion increases with temperature. Up to near the softening-point, the temperature coefficient appears to be linear. Over the softening range (about 40°C.) the rate of expansion increases notably, being from two to seven times the rate prior to softening (*see* Peters and Cragoe, J. Amer. Opt. Soc. 1920, 4, 105).

Apart from the desirability of using low expansion glass for chemical apparatus (beakers and flasks) and heat-resisting illuminating ware, the magnitude of the coefficient of expansion is of importance when two glasses have to be united, as in the 'flashing' process, or when metallic wires have to be sealed into glass. In both cases it is desirable for the two objects to be sealed to have rates of expansion not very far different. The expansion rate of a glass can by modifying its composition be varied over a considerable range so as to provide for the sealing in of metals such as copper and tungsten. This variation of linear thermal expansion may range, approximately, from 30×10^{-7} to 130×10^{-7} (E. C. Sullivan, J. Soc. Chem. Ind. 1916, 35, 51). Lead glasses have been largely used not only for casing or depositing one on the other in layers, but also for sealing in platinum wires. The coefficient of expansion of a normal lead glass containing 20–30 p.c. of lead oxide is not very far removed from that of platinum. There is no doubt, however, that successful casing or sealing-in depends also on the softness or plasticity of the materials to be united, and lead glass possesses this property in a marked degree.

Resistance to Sudden Change of Temperature depends not only on the thermal expansion but also on the specific heat, the conductivity, the density, the tensile and compression strength, and elasticity. The so-called *thermal endurance* can be measured comparatively by heating to a definite temperature glass rods of similar length and diameter within a vertical electric tube furnace and then allowing them to fall into cold water at a definite temperature. Flasks may be compared by charging them with paraffin wax, heating them to a definite temperature and plunging into water at 20°C. Well-annealed Jena flasks have been found to withstand sudden chilling from 250° to 20°, although the range usually observed is not quite so wide. Both the actual thickness and the uniformity of distribution of the glass in a piece of glassware influence the cracking temperature. Common beer bottles containing hot water and immersed in a hot water bath will rarely withstand removal and quenching from 80° C. to 20°C. in cold water.

The thermal conductivity of glasses has been investigated by Winkelmann, by Paalhorn, and by Fochs, but it cannot yet be said that the relationship between composition and thermal composition has yet been worked out satisfactorily. Apparently, increasing the amount of the oxides Al_2O_3, SiO_2, B_2O_3, MgO, and CaO tends to increase the conductivity of the glass, whilst the oxides PbO, ZnO, BaO, and K_2O, on the other hand, most effectively diminish it.

The specific heat of glasses at temperatures 0°–100° can be calculated approximately from the values for the oxides by use of the formula

$$C = \frac{p_1}{100} c_1 + \frac{p_2}{100} c_2 + \frac{p_3}{100} c_3 + \ldots$$

where p_1, p_2, p_3, &c. are the percentage amounts of each oxide, and c_1, c_2, c_3, &c. the specific heats of the oxides, C being the specific heat of the glass. The values for some oxides are SiO_2, 0·191; B_2O_3, 0·227; Na_2O, 0·267; K_2O, 0·186; CaO, 0·190; BaO, 0·067; MgO, 0·244; PbO, 0·051; ZnO, 0·125. Knowledge of the specific heat of glasses at high temperatures is almost entirely lacking (*see* also W. P. White, Amer. J. Sci. 1919, 47, 1).

The density, in the case of glasses of similar constitution, varies in an approximately linear manner with the composition (Larsen, Amer. J. Sci. 1909, 28, 263; Tillotson, J. Ind. Chem. 1911, 3, 897; English and Turner, J. Soc. Glass Tech. 1920, 4, 78, 153). This applies, for example, to the sodium-calcium and sodium-magnesium trisilicate glasses.

In general, the densest commercial glasses are those containing lead, although thallium glasses are still specifically heavier. Lead silicate glass, containing approximately 80 p.c. PbO, has a density of about 6·3. Winkelmann believed the density and composition were so related that $100/D = p_1/d_1 + p_2/d_2 + p_3/d_3 + \ldots$ where D is the density of the glass, p_1, p_2, p_3, &c. the percentages of the several oxides, and d_1, d_2, d_3, &c. the density factors by which the density was increased for each 1 p.c. of oxide. These density factors were, for SiO_2, 2·3; B_2O_3, 1·9; CaO, 3·3; Na_2O, 2·6; PbO, 9·6 (*see*, however, English and Turner, *l.c.*; Baillie, J. Soc. Glass Ind. 1921, 40, 141.)

Young's modulus of elasticity was shown by Winkelmann and Schott to be related to the composition in such a way that if E is the elasticity, $E = a_1Z_1 + a_2Z_2 + a_3Z_3 + \ldots$ where a_1, a_2, a_3, &c. are the percentage amounts of each constituent oxide, and z_1, z_2, z_3, &c. factors which represent the increase of elasticity due to each 1 p.c. of the oxide. These factors were calculated by Winkelmann and Schott, but there is reason to doubt their accuracy; for example, the effect of CaO when replacing Na_2O in a series of trisilicate glasses is to increase greatly the elasticity (J. R. Clarke and W. E. S. Turner, J. Soc. Glass Tech. 1920, 4, 260) whereas Winkelmann and Schott ascribe equal effects to them. For the glass $6SiO_2$, $1·9Na_2O$, $0·1CaO$, E=5930 kg./mm.^{2}; and for $6SiO_2$, $1·1Na_2O$,

$0{\cdot}9CaO$, $E=7249$ kg./mm.^{2}. Zschimmer gives limiting values hitherto found for different glasses as 4800–7970 kg./mm.^{2}. A glass with SiO_2, 66·6 p.c.; CaO, 18·06 p.c., and Na_2O, 12·7 p.c., however, had a value 8343 kg./mm.^{2} (Clarke and Turner, *l.c.*).

Tensile strength has proved in the past not easy to measure with accuracy. Zschimmer quotes limits found for glasses as 3·3–8·1 kg./mm.^{2}. Winkelmann and Schott concluded that an additive relationship existed between composition and tensile strength. Glasses containing CaO and ZnO had highest, and those with Na_2O and K_2O least, tensile strength.

The compression strength is much greater than the tensile strength. The limits quoted by Zschimmer from the observations of various workers are 60·5–126·4 kg./mm.^{2}. According to Winkelmann and Schott, SiO_2, Al_2O_3, MgO, and B_2O_3 effectively increase resistance to compression, whilst the alkalis Na_2O and K_2O as well as BaO reduce it most.

On the viscosity of glass and especially on the change of viscosity with temperature depends its working in practice. Unfortunately, few systematic data have been recorded. Lead glasses are noteworthy as having a long working range, that is, the viscosity changes slowly over the range from 550° to 850°. On the other hand, high CaO content gives fluidity above 1200°, but the glass very rapidly sets when cooled below 1100°. Such glass is therefore advantageous in producing hand-made, thick-walled bottles of considerable size. Magnesia glasses have much higher viscosity than lime glasses at high temperatures. Silica and alumina increase the viscosity. Glasses containing both Na_2O and K_2O work more easily than those with one alkaline oxide only (*see* K. Arndt, Zeitsch. Chem. Apparaterkunde, 1908, 3, 474; V. Veseley, Sprechsaal, 1911, 44, 457; A. L. Feild, Trans. Faraday Soc. 1917, 13, 3; E. W. Washburn, Trans. Amer. Cer. Soc. 1920, 3, 735).

The afterworking of glass is the phenomenon of slow shrinking observed in glass after being reheated. For this reason, a thermometer bulb may show a slight rise of zero with age whilst, if heated, and then cooled fairly quickly, the zero is depressed. The depression constant of a thermometer is the depression observed when heated to 100°C. and cooled fairly quickly to normal air temperature. Weber, in 1883, showed that large depression constants were due to the presence of both Na_2O and K_2O. For thermometer purposes only one alkaline oxide should be present in the glass, and the glass also should not be too soft. Much effort was made by the Jena workers to eliminate or reduce afterworking; two successful glasses, 16 (III) and 59 (III) were made having depression constants of only 0·05° and 0·02° respectively. The French glass *verre dur*, resembling window glass in composition, also has a very low depression constant.

Devitrification is the phenomenon of loss of the glassy or vitreous state. Whilst several changes in glass are sometimes associated with devitrification, the term would perhaps be best confined to the separation out in the crystalline state of some constituent present in excess of the solubility limit. The constituent may be silica or may be a silicate, the former frequently being deposited both from lead and from calcium glasses containing a high proportion of silica. This silica may be, according to the temperature, cristobalite or tridymite, and may give the glass either a mere opalescence or smokiness, or may produce a dense white deposit. Of the silicates, $CaSiO_3$ or wollastonite, is the best known cause of devitrification of soda-lime glasses. $BaSi_2O_5$ from barium crown glasses has also been observed. $PbSiO_3$ is only deposited from glasses containing a very high proportion of PbO. Devitrification depends on the maintenance of the soft glass at a suitable deposition temperature for a sufficient length of time. The viscosity is therefore a most important factor. In this connection, lithium glasses are most readily devitrified, sodium less easily and potassium least of the three alkalis, the viscosity increasing rapidly also in this order, the potassium glasses being most viscous. The addition of certain oxides, as Al_2O_3 and B_2O_3, hinders devitrification, and for this reason the first-named oxide is a constituent of lamp-working (bench glass blowing) glasses, and is a useful addition to sodium calcium glasses which have to be maintained for any considerable time in a fairly plastic state.

The specific electrical resistance is influenced by the state of annealing, well-annealed glass having the higher resistance. The best insulating glasses are usually those most resistant to weathering and chemical attack. Increase of lead in potassium lead silicate glasses increases the electrical resistance. The glass containing SiO_2, 33; Al_2O_3, 6·0; BaO, 48·0; and B_2O_3, 12·0 p.c. is a most efficient insulator. Gray and Dobbie observed that the electrical conductivity of glasses was doubled for each 9°C. rise in temperature (Proc. Roy. Soc. 1898, 63, 38; 1900, 67, 197).

The dielectric constant or specific inductive capacity of glass has been found from observation to be between the limits 5·4–8·5 at ordinary temperature. The effect of composition remains yet to be satisfactorily worked out.

Refractive index is related to density, and the two properties increase or diminish in a parallel manner in similar glasses. Although the composition of glass may vary very widely, the refractive index does not change in so marked a degree as other physical properties. For n_D, the limits for practically all known glasses lie approximately between 1·50 and 1·96. Lead glasses, the densest in general use, have highest refractive index, the glass of density 6·3 (*see* p. 380) having value for n_D of 1·96. The barium glasses come next in order. The optical constants of a glass most frequently used are n_C, n_D, n_F, n_G, the refractive indices for the C, D, F, and G lines of the hydrogen spectrum; the total dispersion defined as (n_F-n_C) and the ratio $\frac{n_D-1}{n_F-n_C}$, designated by the symbol ν. The lead glasses are characterised by high refractive index and dispersion, and consequently low value of ν. Sodium-calcium and potassium-calcium glasses have low refractive index and dispersion, and fairly high ν value. Barium glasses possess high refractive index, low dispersion, and high values of ν. Increase in the content of SiO_2, B_2O_3, Na_2O, or K_2O diminishes the refractive index.

In a series of similarly constituted glasses, such as the sodium-calcium trisilicates, the relationship between composition and refractive index is linear (Larsen, Amer. J. Sci. 1909, 28, 263; Clarke and Turner, J. Soc. Glass Tech. 1920, 4, 111; *see also* C. J. Peddle, J. Soc. Glass Tech. 1920, 4, 1, 299; 1921, 5, 72).

The **absorption of light** is dependent partly on the thickness, but mainly on the composition of the glass, especially in respect of its content of oxides which exercise selective absorption. The best optical glass should transmit 98–99 p.c. of the incident light. On the other hand, unpolished mirror glass, 8 mm. thick, may only transmit about 87 p.c., whilst for glass strengthened by wire mesh, the transmitted light may be only 55–60 p.c. The foregoing refers to general transmission of ordinary white light. In the case of selective absorption, the different coloured oxides vary in the strength of their effect, cobalt oxide being one of the most powerful. The absorption curves for several glasses containing CoO, Cr_2O_3, NiO, Fe_2O_3, and Mn_2O_3 have been measured by Zsigmondy (Ann. Physik. 1901, 4, 60).

The selective absorption varies both with the concentration of the oxide and with the temperature. The general effect of rise of temperature is to shift the absorption towards the red end whilst the amount of absorption may simultaneously be increased. This is illustrated by the following relative transmission factors at different temperatures:

Colouring agent	Colour (1) Cold	Colour (2) Hot	Relative transmission factor 30°	200°	350°
Cu .	Medium red	—	100	92	84
Co .	Light blue	—	100	104	108
Co .	Deep violet	Deep blue	No appreciable change		
Au .	Pink	Violet	100	96	93
Cu .	Bluish-green	Yellowish-green	100	94	82
Mn .	Purple	Bluish-violet	100	94	90
Cu .	Deep red	—	100	67	42
Cr .	Yellowish-green	Yellow	100	84	67

In regard to ultra-violet radiation, fused quartz and fused B_2O_3 are transparent, whilst a mixture of B_2O_3, CaF_2, and Al_2O_3 shows only weak absorption. Heavy lead glasses and glasses coloured slightly with Cr_2O_3 absorb ultra-violet light.

Glasses which absorb heat radiations may be obtained by the use of the oxides or other compounds of chromium, cerium, and iron, and certain other elements. The mineral biotite and the oxide Fe_3O_4 dissolved in soda-lime glass absorb a high proportion of incident heat rays, whilst Crookes prepared a soda-lime glass from a batch containing 10 p.c. of ferrous oxalate which absorbed 98 p.c. of the heat radiations (Crookes, Phil. Trans. 1914, 214, 1).

Classification of Glasses.

As almost all glasses contain silica, and as, moreover, certain metallic oxides such as calcium oxide and sodium oxide, are present in many different types of glass, a simple classification based on composition is not available. Perhaps a better method, by no means a definite system, may be to classify glasses according to their use. In this way, we have the following varieties:

I. Lime-soda glasses for common use. This type of glass is far and away the most important, since bottles of all kinds, window glass, and plate glass are made from it, as well as many articles for domestic use such as the cheaper forms of tumblers and pressed table glassware.

A. *Common bottles and glass containers.* Analyses of actual samples show that considerable diversity of composition exists.

	1	2	3	4	5	6
SiO_2	75·34	73·06	69·73	73·26	69·11	61·90
Na_2O	13·78	15·26	11·22	17·88	11·07	6·16
K_2O .	3·41	0·98	—	—	—	1·13
CaO .	6·83	8·70	17·38	7·24	11·83	17·95
MgO .	0·21	0·17	0·55	0·17	1·58	6·38
Al_2O_3 .	0·45	1·30	0·50	1·31	3·46	4·44
Fe_2O_3 .	0·30	0·30	0·25	0·11	1·82	1·66
MnO .	—	—	—	—	1·13	—
Sb_2O_3	trace	trace	—	—	—	—
As_2O_3 .	—	—	0·47	trace	—	—
Se .	—	—	—	trace	—	—
CoO .	—	—	—	trace	—	—

1. Continental made soda-water syphon.
2. Meat jar.
3. British glass for hand-made bottles.
4. Automatic machine-made bottle of colourless glass
5. Dark green bottle machine-made by O'Neill machine.
6. Champagne hand-made wine bottle.

B. *Pressed glassware* of the cheaper types frequently has a composition somewhat similar to the bottle glass A4.

A considerable improvement in the appearance of pressed table-ware may be obtained by replacing the calcium partly by barium oxide, and the latter is accordingly frequently used.

C. *Window and plate glass* from different sources do not vary greatly in composition, as illustrated by the following figures:

	Window glass French	Window glass German	Plate glass American	Plate glass German	Plate glass French
SiO_2 .	72·1	72·68	71·5	72·5	71·3
Na_2O .	12·2	13·24	13·7	13·8	10·4
K_2O .	—	—	—	0·2	0·4
CaO .	15·7	12·76	12·4	11 5	14·7
MgO .	—	0·26	—	—	—
Al_2O_3 . Fe_2O_3 .	traces	1·06	0·1	0·1	0·4
As_2O_3 .	—	—	0·1	—	—
Sb_2O_3 .	—	—	—	0·5	—

D. *Illuminating glassware.* A good deal of the common illuminating ware such as lamp chimneys and globes and shades is made from a calcium-sodium or calcium-sodium-potassium glass, with or without other oxides. Calcium-sodium glass containing magnesium has come into extended use for the manufacture of electric light bulbs, replacing the more expensive lead glass. Common machine-made globes

$0·9CaO$, E=7249 kg./mm.². Zschimmer gives limiting values hitherto found for different glasses as 4800—7970 kg./mm.². A glass with SiO_2, 66·6 p.c.; CaO, 18·06 p.c., and Na_2O, 12·7 p.c., however, had a value 8343 kg./mm.² (Clarke and Turner, *l.c.*).

Tensile strength has proved in the past not easy to measure with accuracy. Zschimmer quotes limits found for glasses as 3·3–8·1 kg./mm.². Winkelmann and Schott concluded that an additive relationship existed between composition and tensile strength, Glasses containing CaO and ZnO had highest. and those with Na_2O and K_2O least, tensile strength.

The compression strength is much greater than the tensile strength. The limits quoted by Zschimmer from the observations of various workers are 60·5–126·4 kg./mm.². According to Winkelmann and Schott, SiO_2, Al_2O_3, MgO, and B_2O_3 effectively increase resistance to compression, whilst the alkalis Na_2O and K_2O as well as BaO reduce it most.

On the viscosity of glass and especially on the change of viscosity with temperature depends its working in practice. Unfortunately, few systematic data have been recorded. Lead glasses are noteworthy as having a long working range, that is, the viscosity changes slowly over the range from 550° to 850°. On the other hand, high CaO content gives fluidity above 1200°, but the glass very rapidly sets when cooled below 1100°. Such glass is therefore advantageous in producing hand-made, thick-walled bottles of considerable size. Magnesia glasses have much higher viscosity than lime glasses at high temperatures. Silica and alumina increase the viscosity. Glasses containing both Na_2O and K_2O work more easily than those with one alkaline oxide only (*see* K. Arndt, Zeitsch. Chem. Apparaterkunde, 1908, 3, 474; V. Vesceley, Sprechsaal, 1911, 44, 457; A. L. Feild, Trans. Faraday Soc. 1917, 13, 3; E. W. Washburn, Trans. Amer. Cer. Soc. 1920, 3, 735).

The afterworking of glass is the phenomenon of slow shrinking observed in glass after being reheated. For this reason, a thermometer bulb may show a slight rise of zero with age whilst, if heated, and then cooled fairly quickly, the zero is depressed. The depression constant of a thermometer is the depression observed when heated to 100°C. and cooled fairly quickly to normal air temperature. Weber, in 1883, showed that large depression constants were due to the presence of both Na_2O and K_2O. For thermometer purposes only one alkaline oxide should be present in the glass, and the glass also should not be too soft. Much effort was made by the Jena workers to eliminate or reduce afterworking; two successful glasses, 16 (III) and 59 (III) were made having depression constants of only 0·05° and 0·02° respectively. The French glass *verre dur*, resembling window glass in composition, also has a very low depression constant.

Devitrification is the phenomenon of loss of the glassy or vitreous state. Whilst several changes in glass are sometimes associated with devitrification, the term would perhaps be best confined to the separation out in the crystalline state of some constituent present in excess of the solubility limit. The constituent may be silica or may be a silicate, the former frequently being deposited both from lead and from calcium glasses containing a high proportion of silica. This silica may be, according to the temperature, cristobalite or tridymite, and may give the glass either a mere opalescence or smokiness, or may produce a dense white deposit. Of the silicates, $CaSiO_3$ or wollastonite, is the best known cause of devitrification of soda-lime glasses. $BaSi_2O_5$ from barium crown glasses has also been observed. $PbSiO_3$ is only deposited from glasses containing a very high proportion of PbO. Devitrification depends on the maintenance of the soft glass at a suitable deposition temperature for a sufficient length of time. The viscosity is therefore a most important factor. In this connection, lithium glasses are most readily devitrified, sodium less easily and potassium least of the three alkalis, the viscosity increasing rapidly also in this order, the potassium glasses being most viscous. The addition of certain oxides, as Al_2O_3 and B_2O_3, hinders devitrification, and for this reason the first-named oxide is a constituent of lamp-working (bench glass blowing) glasses, and is a useful addition to sodium calcium glasses which have to be maintained for any considerable time in a fairly plastic state.

The specific electrical resistance is influenced by the state of annealing, well-annealed glass having the higher resistance. The best insulating glasses are usually those most resistant to weathering and chemical attack. Increase of lead in potassium lead silicate glasses increases the electrical resistance. The glass containing SiO_2, 33; Al_2O_3, 6·0; BaO, 48·0; and B_2O_3, 12·0 p.c. is a most efficient insulator. Gray and Dobbie observed that the electrical conductivity of glasses was doubled for each 9°C. rise in temperature (Proc. Roy. Soc. 1898, 63, 38; 1900, 67, 197).

The dielectric constant or specific inductive capacity of glass has been found from observation to be between the limits 5·4–8·5 at ordinary temperature. The effect of composition remains yet to be satisfactorily worked out.

Refractive index is related to density, and the two properties increase or diminish in a parallel manner in similar glasses. Although the composition of glass may vary very widely, the refractive index does not change in so marked a degree as other physical properties. For n_D, the limits for practically all known glasses lie approximately between 1·50 and 1·96. Lead glasses, the densest in general use, have highest refractive index, the glass of density 6·3 (*see* p. 380) having value for n_D of 1·96. The barium glasses come next in order. The optical constants of a glass most frequently used are n_C, n_D, n_F, n_G, the refractive indices for the C, D, F, and G lines of the hydrogen spectrum; the total dispersion defined as $(n_F - n_C)$ and the ratio $\frac{n_D - 1}{n_F - n_C}$, designated by the symbol ν. The lead glasses are characterised by high refractive index and dispersion, and consequently low value of ν. Sodium-calcium and potassium-calcium glasses have low refractive index and dispersion, and fairly high ν value. Barium dense flints, extra dense flints, light barium flints, and so on.

The percentage composition of some types is stated in the following table:

	Light flint	Medium flint	Dense flint	Very dense flint	Barium flint
SiO_2 .	53·9	44·1	39·0	20·0	53·69
PbO .	36·7	44·7	49·0	79·9	16·71
K_2O .	6·0	9·8	4·0	—	8·31
Na_2O .	1·0	1·2	3·0	—	1·69
BaO .	—	—	—		14·27
CaO .	1·96	—	4·0	—	—
ZnO .	—	—	—	—	2·68
B_2O_3 .	—	—	—	—	—
As_2O_3 .	0·3	0·2	0·2	0·1	2·53
Sb_2O_3 .	—	—	1·0	—	—
n_D .	1·5803		1·6068	1·6555	
n_C .	1·5762		1·6022	1·6502	
n_F .	1·5902		1·6184	1·6692	
n_G .	1·5986		1·6281	1·6800	
ν .	41·0		37·5	34·4	

	Light crown	Boro-silicate crown	Light barium crown	Dense barium crown	Phos-phate crown
SiO_2 .	68·5	68·2	48·1	39·6	(P_2O_5) 70·5
PbO .	—	—	—	3·0	—
K_2O .	5·0	9·5	7·5	—	12·0
Na_2O .	12·0	10·0	1·0	—	—
CaO .	—	—	2·0	2·0	—
BaO .	9·7	—	28·3	44·0	—
B_2O_3 .	3·5	10·0	4·5	5·0	3·0
As_2O_3 .	0·2	0·2	0·4	0·4	0·5
Al_2O_3 .	—	—	—	—	10·0
ZnO .	1.0	2·0	—	7·7	—
Mn_2O_3 .	—	0 06	—	—	—
MgO .	—	—	—	—	4·0
n_D .	1·5179		1·5615	1·5905	
n_C .	1·5153		1·5568	1·5874	
n_F .	1·5138		1·5683	1·5977	
n_G .	1·5286		1·5837	1·6036	
ν .	60·9		58·1	57·0	

5. **Coloured glass.** The range of colours which it is possible to impart to glass is very great. If we include white or opal, it is possible to divide the coloured glasses into groups according to the origin of the colour.

(a) *Coloured silicates.* A number of oxides produce coloured silicates. Cobalt oxide produces a silicate which is blue. From a similar cause probably arise the following colours—Green: ferrous oxide, uranium oxide (fluorescent), chromium oxide, and (at high temperature) manganese oxide. Blue: cobalt oxide and copper oxide (the latter under oxidising conditions). Pink or purple: manganese oxide, nickel oxide.

(b) *Colour due to colloidal solution or suspension.* The ruby colours due to gold, copper, or selenium, are good examples. Each reagent is added to the batch mixture as a salt, accompanied by a reducing agent (although the selenium may be added as such or may be reduced by the furnace flame alone). When first made, the glasses are either colourless or have a light straw colour, but, on reheating, the ultra-microscopic particles of gold, copper, or selenium, grow larger by segregation leading to the production of the ruby colour. If the last treatment is continued, the colour will ultimately become brown and finally visible particles of gold appear, resulting in the production of *aventurine* glass.

Amber colours, due to colloidal carbon and possibly also producible by colloidal sulphur; and yellow, due to silver, are further examples.

(c) *Opals produced by separation of an emulsion.* The calcium phosphate (bone-ash) opals, appear to be due to this cause, the phosphate dissolving initially at high temperature and being precipitated from solution at a lower.

(d) *Opals produced by inclusion of air or gas bubbles.*

(e) *Opals produced by devitrification.* The devitrification may be due to deposition of silica, when the effect may vary from a mere cloudiness or smokiness to actual opalescence. Opal may also be formed by the separation of masses of $CaSiO_3$ or other silicates in very small crystals.

THE RAW MATERIALS FOR GLASSMAKING.

The raw materials for glassmaking may be classified as—

I. Fundamental materials, or those which yield the acid and basic oxides comprising the main substance of the glass: SiO_2, B_2O_3, P_2O_5, Al_2O_3, Na_2O, K_2O, Li_2O, CaO, MgO, PbO, BaO, ZnO, FeO, and Fe_2O_3.

II. Fluxes: As_2O_3, Sb_2O_3, B_2O_3, $Na_2B_4O_7$, CaF_2, K_2SiF_6, $NaNO_3$, KNO_3.

III. (a) Colouring agents: CuO, FeO, CaO, MnO_2, Se, C, S, $AuCl_3$.

(b) Decolorisers: MnO_2, Se, As_2O_3, Sb_2O_3, NiO.

(c) Opacifiers: SnO_2, $Ca_3(PO_4)_2$, Na_3AlF_3, ZrO_2, As_2O_5.

IV. Oxidising agents: $NaNO_3$, KNO_3, BaO_2, Pb_3O_4, MnO_2.

V. Reducing agents: C (as coal, coke, or other form of carbon), Zn, Rochelle Salt, SnO.

It is to be understood that the basic oxides referred to above are generally used in the form of their salts. Only the more important materials are commented on in the section which follows.

ACID OXIDES AND THEIR SOURCES.

Silica. Sand constitutes the only really important source of the silica which is present, in the majority of lead glasses, to at least 55 p.c., and in calcium and other glasses to not less than 66 p.c. The degree of purity demanded in a sand varies with the type of glass to be made. Iron oxide is the impurity least desired by the glass manufacturer. It may be present as hydrated oxide, limonite ($Fe_2O_3H_2O$) or may be associated with clay material, in both of which cases it may be reduced by washing; or again, a definite iron-containing mineral, such as ilmenite, in which case separation is difficult.

For optical glass, the amount of iron oxide (as Fe_2O_3) should not exceed 0·03 p.c.; for the best table-ware, not exceeding 0·05 p.c.; for second grade table-ware and chemical glassware up to 0·08 or even 0·1 p.c.; window glass 0·15 to 0·25 p.c.; for dark-green bottle glass, as much as 2–3 p.c. or even more. For practical purposes, there are no workable deposits of sand in the United Kingdom capable of satisfactory use for good optical or the best table-ware glass. Excellent sands are found in France at Fontainebleau; in Germany at Hohenbockaer and Nivelstein; in the United States at Berkeley Springs, West Virginia, and at Ottawa, Illinois, with good sands also at various locations in Pennsylvania, New Jersey, and Massachusetts. Belgium has excellent sand. The best British sands, at present, come from King's Lynn, Aylesbury, and Leighton Buzzard.

The following table states the composition of samples examined:—

Sand	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	Loss on ignition	Remarks
Fontainebleau	99·62	0·163	0·017	—	0·02	trace	—	—	0·12	—
Belgian .	98·64	0·63	0·06	—	0·31	0·13	0·45	trace	0·12	—
Lynn (Boam's double washed)	98·82	0·56	0·08		0·16	0·02	—	—	0·33	—
Aylesford .	99·33	0·31	0·12	trace	0·04	trace	0·22	trace	0·12	—
Waen . .	98·63	0·41	0·03	—	0·16	—	0·20	trace	0·28	Crushed rock
Kinghorn .	92·92	1·50	1·38	trace	1·90	0·60	Not determined		1·32	—
Fauldhouse .	98·67	1·02	0·13		Not determined				—	Crushed rock *
Worksop .	95·10	2·32	0·51	trace	0·22	0·24	1·07	(By diff.)	0·54	—
Muckish Mt. .	99·55	0·17	0·02	Not determined	0·20	trace	—	—	0·16	Crushed rock
Ottawa, Ill. .	99·48	0·16	0·02	—	0·11	0·05	—	—	0·13	—
Berkeley Springs .	99·65	0·11	0·02	—	0·12	trace	-	—	0·23	—
Hohenbockaer	99·71	0·04	0·014		—	0·005	0·04	—	0·04	—
Nievelstein .	99·97	—	0·009	-	0·01	0·006	-	-	—	—

* White variety.

For optical glass, and, generally speaking, for the finest table-ware glass, impurities should be absent as far as possible, and the percentage of silica reach 99·5 p.c. Except for iron oxide, the other impurities may even be an advantage in the glass when optical glass is not in preparation, whilst the iron oxide is a useful constituent when dark bottle glass is to be made.

The size of the sand grain is also of importance. No particles should be incapable of passing a 20-mesh sieve, and a good sand is one which consists mainly (more than 90 p.c.) of particles between 30 and 70-mesh. The coarse particles are difficult to melt; the very fine material contains a great proportion of impurity and may entrap fine air bubbles.

Boric oxide is added variously as borax, boric acid H_3BO_3, and as oxide, B_2O_3, the first-named being usable only when the glass contains sufficient sodium oxide to permit part of it to be introduced as borax. The oxide is usually too expensive. Boric oxide bestows great resistance to corrosion by water, and a small amount (1 p.c.) greatly improves lead table-ware glass in this respect, whilst the best glass for water gauges and chemical ware also contains it as an essential constituent. It serves as a valuable flux and is a good solvent for colouring materials. Accordingly, some colours which are due probably to colloidal solution are not readily developed in presence of boric oxide.

Phosphoric oxide in any considerable amount is rarely met with. It is employed in special optical glasses (*e.g.* phosphate crowns) intended for use in protected portions of optical apparatus. Most phosphate glasses are readily attacked by atmospheric moisture and weathering agencies.

It is also used in small amounts in glass for table-ware as it bestows on it a bright appearance. For such a purpose it has sometimes been added as bone ash but may better be added as sodium phosphate (Na_2HPO_4). For optical glass, meta-phosphoric acid is the form employed. Phosphate glasses, in which the chief acid oxide is silica, are the opal glasses produced by the addition of bone ash or calcium phosphate (p. 388).

Arsenious oxide (As_2O_3) (technically 'arsenic') and antimony oxide (Sb_2O_3) may be classified under the acidic oxides. Alumina probably also exercises an acidic function, but it is dealt with below under basic oxides.

BASIC OXIDES.

Calcium compounds. Calcium may be added as carbonate, oxide, or hydrated oxide. Precipitated carbonate and powdered calcite (limespar) are used where impurities must be excluded, whilst chemical lime and soap waste (both industrial by-products) as well as limestone, are used for common bottle glass. Burnt lime is largely used in American glass practice; slaked lime is used occasionally in Great Britain.

Unless for common bottle glass, the impurity to be avoided is iron oxide. Precipitated calcium carbonate usually has negligible quantities of iron oxide, alumina, and silica; limespar may have larger amounts of each of these impurities, and the iron may to some extent be introduced during the grinding of the limespar. When used for ordinary white glass, the iron oxide content should not exceed 0·1 p.c. In the limestones, organic matter and some phosphate may be present. Magnesia may or may not be considered as an impurity. In some cases it is deliberately added as dolomite limestone, in America as burnt dolomite.

Calcium carbonate in one of its various forms has the advantage of evolving gas during the glass-melting operations, thus assisting to stir up the molten material. Burnt lime must be used quickly owing to its absorption of moisture and carbon dioxide; to a smaller degree slaked lime deteriorates also. On the other hand, burnt lime appears to dissolve more quickly than limestone in sodium carbonate and it is also free from organic matter.

Sodium compounds are introduced as sodium carbonate (technically soda ash), sodium sulphate ('Saltcake'), sodium nitrate (technically 'soda nitre' and 'Chili nitre') and borax. All of these serve as a source of sodium oxide for the glass, and the remainder of the salt escapes as a gaseous product except in the case of borax which also serves as a source of boric oxide.

For all practical purposes, the soda ash employed is manufactured by the ammonia-soda process. It may be 'dense alkali' or 'light alkali' dependent on its specific gravity. The former is preferable.

The impurities are sodium chloride and small amounts of iron oxide and sodium sulphate. Soda ash is one of the most trustworthy products a glass manufacturer has to deal with.

Sodium sulphate or saltcake has had a great vogue in making bottle glass in Great Britain until recently, whilst both in this country and abroad it is largely used for making window glass. It is the custom to add powdered coal or coke, about 5 p.c. of the weight of the saltcake, in order to assist in the reduction of the latter. Some manufacturers, however, work the furnace at a high temperature and rely on the reducing action of the furnace flame entirely. Whilst this is possible in a tank furnace and, to some extent with open pots, a reducing agent must certainly be used if saltcake is in whole or part employed in closed pot operations.

Ordinary samples of saltcake are much less pure than sodium carbonate, and may contain sodium chloride, sodium bisulphate, iron oxide, calcium sulphate, insoluble matter, and moisture as the chief impurities. A good average sample should contain 91-95 p.c. of actual sodium sulphate. Samples yielding only 85 p.c. have not infrequently been met with.

Saltcake was, prior to 1915, much cheaper than soda ash and was used for this main reason. Generally speaking, glass takes longer to prepare when made from saltcake than from soda ash, whilst saltcake is more corrosive of furnace blocks than soda ash.

Sodium nitrate melts easily and therefore serves as a flux, whilst as an oxidising agent it prevents lead oxide in lead batches from being reduced to metallic lead and also hinders the development of the green ferrous silicate. It is added only in conjunction with sodium carbonate; that is, it provides only the minor proportion of the total sodium oxide content.

Borax, as $Na_2B_4O_7$, is a very useful flux, whilst it serves also as a source of boric oxide. It seldom provides more than a small proportion of the total sodium oxide.

Potassium compounds. Potassium carbonate is the chief. It may be added as K_2CO_3 or (to a much smaller extent nowadays) as the hydrated form $K_2CO_3H_2O$. The usual impurities are small amounts of potassium chloride and sulphate. Russian potash often contains several per cent. of chloride and sulphate, leading to the production of opalescence in lead glasses. Potassium nitrate is used for similar reasons to sodium nitrate and in like proportions. For chemical glassware, where the presence of alumina is also desired, potassium may conveniently be added in the form of potash felspar (orthoclase) $K_2O,Al_2O_3,6SiO_2$.

Lead is generally introduced as red lead, Pb_3O_4, but sometimes as litharge. Lead disilicate has been used to a smaller extent. The darker variety of red lead, containing an appreciable amount of PbO_2, is preferred by some glass manufacturers.

Barium compounds. Barium carbonate is the only one in extensive use.

Zinc is added in the form of carbonate.

Aluminium is added in various forms. It is generally present in smaller or larger amounts in the sand used and in the other raw materials. It is also absorbed in small amounts from the fireclay material of which the glass pots or the tank furnace blocks are made. For good colourless glass, aluminium may be added as hydrated oxide, Al_2O_3, H_2O, or as calcined oxide, Al_2O_3, felspar, lepidolite, and china clay of low iron oxide content. China clay has the disadvantage of being less easy to incorporate in the batch than the other forms mentioned.

For common bottle glass, ground bricks or tiles, or even dried raw clay, have been used as sources of alumina.

Opal glass is frequently made by the addition of cryolite, Na_3AlF_6.

Alumina bestows mechanical strength and resistance to chemical corrosion on glass. The addition of small amounts (1 p.c. of the total batch) may make melting easier, but beyond 5 p.c., fusion needs a hot furnace, and with 10 p.c. the glass is not easy to work.

Colouring Agents.

These have already been enumerated. Cobalt is added either as the pure oxide, or, since its colouring power is great, in a diluted form, such as by powdered blue, zaffre (an impure basic cobalt arsenate), or smalt (a glass made from powdered quartz, potassium carbonate, and cobalt oxide, containing about 2-7 p.c. of cobalt oxide. This glass is ground fine for use). Used alone, the oxide imparts a blue colour; with manganese dioxide a violet colour; and added in small quantities to copper and gold glasses, a bluish cast is given to the red colour. Cobalt oxide produces a faint blue colour when present to the extent only of 1 in 100,000 of glass. One part per 1000 produces a deep blue.

Copper for the production of blue glasses may be added as oxide CuO or nitrate. When added as sulphate (copper vitriol) a greenish-blue colour is obtained. For copper ruby glasses, either the red oxide Cu_2O or black oxide CuO is used, in the presence of some reducing agent. In conjunction with chromium compounds, various shades of green may be obtained.

Chromium is employed most frequently in the form of oxide Cr_2O_3, and potassium chromate or dichromate. Care has to be taken, especially with the oxide, to mix thoroughly with the batch owing to limited solubility. In lead glasses a lemon-yellow, and in calcium glasses a greenish-yellow colour is obtained. Barium chromate and copper chromate have also been used.

Uranium, producing a greenish-yellow colour in lead glasses and a fluorescent greenish-yellow in calcium glasses, is used in the form of sodium uranate $Na_2U_2O_7,2H_2O$.

Manganese dioxide is the only manganese compound employed, usually in the form of the mineral pyrolusite. Under oxidising conditions, it produces a purple colour with sodium and a violet with potassium glasses. Used in conjunction with ferric oxide, varying shades of red, brown, and purple may be obtained, dependent on the relative amount and total amount of the two oxides, and, on the presence of oxidising or reducing conditions.

Nickel oxide produces a violet colour in potassium and red-brown in sodium glasses.

Selenium, used either in the form of the element or as the selenite in conjunction with a reducing agent, for example, arsenious oxide, gives rise to various shades of red varying from pink to ruby.

Decolorisers and the decolorising of glass. Within narrow limits of iron oxide content, the greenish colour produced by ferrous oxide can be removed by decolorisers. Oxidising agents such as sodium and potassium nitrates tend to retain or to produce the higher ferric state of oxidation which has but slight colour, namely, straw or yellow. Arsenious oxide, which is readily reduced, assists in the oxidation of carbonaceous matter which would otherwise reduce the iron to the ferrous condition.

The usual decolorising agents, however, are those which when present alone are colouring agents, namely, manganese dioxide, nickel oxide, and selenium. Potassium glass containing the first-named oxide shows most marked absorption in the yellow and green part of the spectrum, the red and violet being transmitted. A glass with iron oxide, on the other hand, transmits green and yellow to the greatest extent, whilst the red and blue show absorption. When the two oxides are present in small amounts simultaneously, they each absorb what the other transmits, resulting in a slight general absorption only. Although the resulting glass may appear colourless, the reduction in the light transmitted tends to create a dull or greyish appearance. For optical glass, raw materials with very low iron oxide content are used so as to avoid the necessity of adding a decoloriser. Manganese dioxide does not perfectly decolorise sodium glasses, a brownish tinge being left, which is removed when a minute amount of cobalt oxide is added with the manganese dioxide.

Manganese dioxide needs to be used under oxidising conditions, and is therefore suitable for closed pot operations. Nickel oxide is not affected by the furnace atmosphere. It is frequently used with 5–7 p.c. of its weight of cobalt oxide in sodium glasses. Selenium needs a reducing atmosphere, making it very suitable for tank furnace practice. It is usually employed in conjunction with 10–50 times its own weight of arsenious oxide.

The Glass Batch.

General composition. A number of attempts have been made to establish a definite relationship between the basic and acidic oxides of a stable glass. The simple, two component glasses composed of the sodium silicates (*Water glasses*, see later) are not sufficiently stable for the manufacture of glassware. The introduction of a di- or trivalent oxide, such as CaO, PbO, or Al_2O_3, brings about a large increase in stability. Most commercially successful glasses contain at least three components. Benrath came to the conclusion from the examination of a number of good glasses on the one hand and faulty on the other, that, with the special exception of certain optical glasses, the normal composition of satisfactory alkali-lime-lead oxide glasses should vary between the limits

$$Na_2(K_2)Si_3O_7 + Ca(Pb)Si_3O_7$$

and $5Na_2(K_2)Si_3O_7 + 7Ca(Pb)Si_3O_7$.

Tscheuschner about ten years later (1885) deduced the following formula for a good glass containing the alkalis and alkaline earths, namely $xA + yE + 3\left(\frac{x}{y} + y\right)SiO_2$, where xA represents the number of equivalents of the total alkalis Na_2O and K_2O, yE of the alkaline earth oxides.

More recently still, Koerner (1915) has arrived at the conclusion that in lime-containing glasses, the proportion of silica should be greater when potash is present than is required for soda. Thus, when one equivalent of lime is present (*i.e.* $y=1$), the proportion of SiO_2 needed is $4(x^2+1)$. If both soda and potash are present, x representing the total equivalent of the alkaline oxides, and xK represents that of K_2O, the amount of SiO_2 needed is $\left(3+\frac{xK}{x}\right)(x^2+1)$.

Certainly it is true that a calcium glass of the composition $6SiO_2$, CaO, Na_2O shows great stability, and many of the commercial calcium-containing glasses, may, very approximately, be represented by the so called trisilicate formula, in which, for each $3SiO_2$, the CaO does not fall below 0·3 molecule.

Whilst experience in the past appears to have led to this adoption of a trisilicate formula, it does not follow that for modern methods of treatment, it gives the most suitable glass. Peddle recommends a sodium-calcium-containing glass of composition $5SiO_2$, CaO, Na_2O for many types of hollow ware. Pyrex glass, on the other hand, even contains 92 p.c. of acidic oxides.

Preparation of the batch. In modern plants specialising in the production of a limited variety of articles, such as bottles, the various raw materials are stored in large, cylindrical concrete tanks, arranged in a row, and at an elevation from the ground sufficient to permit of a truck or waggon to run beneath and collect from each bin the required quantity of material for the mixture or batch. In one system, a weighing machine mounted on a motor-driven truck propelled along a track below the storage tanks, carries a cylindrical drum. By means of a series of indicators set by the management, several materials may be weighed separately into the drum, and when the required amounts have been obtained the drum is rotated by a second motor and the batch thoroughly mixed. It is then emptied down a grating on to a conveyor belt which carries it to hoppers suspended over the feeding end of the furnace. It is possible, by such a system, for one man to mix sufficient batch to maintain six large tank furnaces in continuous operation.

In other, simpler systems, the materials are weighed out into a truck and emptied into a mixing machine such as the Smith mixer, specially made for the purpose, consisting of a short cylinder with truncated conical ends, like some types of concrete mixer.

Where the number of types of glassware made in a factory is so large that many different batches have to be made up, as in certain pot-furnace works, a correspondingly small mixing plant is used, and may consist merely of a rectangular box rotating on an axis passing through one diagonal, or even of a simple barrel. Hand mixing is often still employed, the materials being weighed out into a wooden vat and mixed by a wooden scoop or shovel.

Batches for different types of glass. The following batches will serve to indicate the general proportions of the various constituents used in making different glasses, especially illustrating the amounts of colouring, opacifying, or decolorising materials required. Whilst they have actually been employed in practice, it does not follow that the batches represent the best possible for any particular type of operation.

The terms soda ash and potash, used below, correspond to anhydrous sodium carbonate (58 p.c. alkali) and potassium carbonate respectively.

I. Lime-containing glasses.

A. *Bottles.*

1. *Quick-setting glass for large hand-made beverage bottles.* Sand 1000, limestone 500, soda ash 300, saltcake 100.

2. *For Owens' machine.* Sand 1000, soda ash 375, limestone 175.

3. *O'Neill's and similar machines.*

(*a*) *Colourless.* First-grade sand 1000, soda ash 375, limespar 170, borax 1, arsenious oxide 1, powdered blue 0·06, selenium 0·03.

(*b*) *Amber-coloured glass.* Sand 1000, soda ash 380, limestone 180, saltcake 8, carbon (as coal or coke) 10, graphite 1.

B. *Cheap glass for common pressed tumblers.*

1. White sand 1000, soda ash 400, limespar 180, arsenious oxide 1, selenium 0·03.

2. *Medium quality glass tumblers.* Sand 1000, soda ash 300, potash 50, limespar 100, baryta 100, potassium nitrate 50, manganese dioxide 2.

C. *Window glass.*

1. Sand 1000, soda ash 260, saltcake 60, limestone 370.

2. Sand 1000, saltcake 420, limestone 300, powdered anthracite 17·5.

II. Lead-containing glasses.

A. *Best crystal glass for table-ware* (*English crystal*).

1. Fontainebleau (or equal grade) sand 1000, potash 330, borax 30, potassium nitrate 40, red lead 660, arsenious oxide 2·5, manganese dioxide 2.

2. *Semi-crystal.* Fontainebleau (or equal grade) sand 1000, potash 350, limespar 140, red lead 100, nickel oxide 0·02.

B. *Electric light bulbs.*

1. Fontainebleau sand 1000, soda ash 330, red lead 480, borax 90, felspar 70, sodium nitrate 50, manganese dioxide 2.

2. Fontainebleau sand 1000, soda ash 140, potash 200, red lead 160, limespar 120, manganese dioxide 0·5, nickel oxide 0·02.

III. Chemical, general scientific, and illuminating glassware.

A. *Glass tubing for general chemical purposes.*

Lynn double-washed sand 1000, felspar 367, limespar 220, soda ash 448, potash 151, magnesia 4, manganese dioxide 2·75.

B. *Beakers, flasks, &c.*

Lynn double-washed sand 1000, hydrated alumina 188, limespar 182, magnesia 15, potassium nitrate 30, soda ash 150, calcined borax 185.

IV. Optical glass.

Such glasses are designed to meet certain specific requirements of refractive index and dispersion, and the batches for these must be arranged accordingly. Thus, an ordinary crown glass of approximate refractive index $n_D = 1·517$, and ν value 60·0 may be obtained from the following batch: Sand (high grade) 1000, potash 420, limespar 265, arsenious oxide 5; whilst a medium flint of $n_D = 1·605$ and $\nu = 37·6$ may be prepared from: Sand (high grade) 1000, potash 103, potassium nitrate 78, soda ash 154, lead oxide (PbO) 884, arsenious oxide 6. The variety of batches for optical glass is very great.

V. Coloured glass.

A. *White, alabaster, or opal.*

1. *Alabaster.* Sand 1000, red lead 560, soda ash 490, sodium nitrate 50, sodium chloride 50, sodium fluoride 75, alumina calcined 225, felspar 1200, antimony oxide 5.

2. *Cryolite opal.* Sand 1000, soda ash 230, potash 40, cryolite 100, felspar 100, fluorspar 100, arsenious oxide 5.

3. *Bone-ash opal.* Sand 1000, potash 300, soda ash 70, bone ash 300, limespar 100.

4. *Milk white glass for lamp shades.* Sand 1000, soda ash 150, felspar 180, fluorspar 90, cryolite 80, tin oxide (SnO_2) 40.

B. *Black glass.*

Sand 1000, potash 100, soda ash 250, limespar 150, manganese dioxide 100, copper oxide 80, cobalt oxide 40, hammer scale (Fe_3O_4) 40.

C. *Red glass.*

1. *Gold ruby.* Sand 1000, red lead 440, potash 290, borax 200, gold chloride 0·36.

2. *Copper ruby.* Sand 1000, potash 200, red lead 300, cupric oxide 3, stannous oxide 1.

In both these cases the ruby colour is only developed on reheating the glass at the mouth of the furnace.

D. *Yellow glass.*

1. *Amber yellow.* Sand 1000, soda ash 250, potash 100, limespar 160, sulphur 15, arsenious oxide 5.

2. *Orange yellow.* Sand 1000, potash 120, soda ash 190, limespar 145, potassium nitrate 5, uranium oxide 3, selenium 0·6, arsenious oxide 2·5.

3. *Canary yellow* (*opal*). Sand 1000, potash 300, red lead 150, limespar 90, potassium nitrate 50, calcium phosphate 30, borax 15, sodium sulphide 7·5, Rochelle salt 7·5, cadmium sulphide 30.

E. *Green.*

1. *Vegetable green.* Sand 1000, soda ash 320, limespar 180, potassium chromate 6·5, hammer scale 4, arsenious oxide 4.

2. *Golden green.* Sand 1000, potash 100, soda ash 200, burnt lime 140, red lead 3, cupric oxide 5, uranium oxide 12·5, arsenious oxide 5.

3. *Aventurine green.* Sand 1000, soda ash

350, felspar 220, fluorspar 100, barium carbonate 180, potassium dichromate 120, manganese dioxide 60.

F. *Blue.*

1. *Dark blue.* Sand 1000, soda ash 350, limespar 160, cobalt oxide 2.

2. *Aquamarine blue.* Sand 1000, potash 50, soda ash 250, limespar 16, copper vitriol 20.

3. *Azure blue.* Sand 1000, potash 200, limespar 120, cryolite 120, copper vitriol 45, smalt 5.

Sand of high grade is desirable in most cases for producing coloured glasses.

Any batch taken from a list such as the above may require adjustment to suit the article for which it is to be worked and the normal temperature of the furnace. The colour also depends on: (1) the freedom of the sand or other raw materials from iron oxide; (2) the presence of oxidising or reducing conditions; (3) the nature of the other constituents present. Thus, as previously indicated, the same colouring agent frequently yields somewhat different colours according as the glass contains lead or calcium, or according as the alkaline element is sodium or potassium.

In general, closed pots are most suitable for coloured glasses, although cobalt blue, iron oxide green, vegetable green, and certain shades of amber can be made successfully in tank furnaces.

In addition to the raw materials stated above, it is usual to add a proportion of previously melted glass or cullet. The amount may vary between 20 and 35 p.c. of the weight of the raw batch. Whatever amount is used it should be kept constant.

THE MELTING OF GLASS.

Glass is melted in clay pots or crucibles, in a pot furnace or in a tank furnace.

Pot furnaces. Pot furnaces are employed for the manufacture of table-ware glass, plain and coloured, and optical glass, and generally in factories where a number of different types of glass are made simultaneously. They are used for making glass of the highest quality.

A pot furnace may hold any number of pots from two to eighteen, and these may contain from about 4 to 30 cwts. of glass. The floor or 'siege' consists of thick fireclay blocks, and its shape may be circular, oval, or rectangular. Rising from the floor are arches, the pillars of which are of fireclay or silica bricks, and the arch is of such dimensions as to accommodate a pot of definite size. A curved roof of silica bricks called the 'crown' completes the enclosure. The understructure depends on the mode of firing adopted. In the old direct-fired, and the semi-gas-fired system, a circular firebox is built below the furnace opening into a circular hole in the siege called the 'eye' through which flame passes from a coal fire, or round which combustion of gas should begin to reach an advanced stage.

Modern furnaces are of two types, recuperative and regenerative, both fired by producer gas.

Figs. 1 and 2 show two vertical sections of the Hermansen type of recuperative furnace. The firing is by means of producer gas generated in the producer P, which forms part of the understructure of the furnace. The gas rises to the eye E, and is mixed with the secondary preheated air which enters the shaft just below the eye at B. The preheating of the air is accomplished in a series of rectangular fireclay tubes, the ends of which are seen in Fig. 2. These tubes are made and put together in such a way as to constitute one set, the ends of which are seen, giving exit to waste hot gases, and a second series at right angles for the air. The waste gases from the furnace are divided into two streams which pass, one into each recuperator, through the tubes and downwards into the main channel leading to the chimney. The air enters at the base of the recuperator, and following a course at right angles to the spent gas, rises, and becomes hotter and hotter. It finds its way out at B.

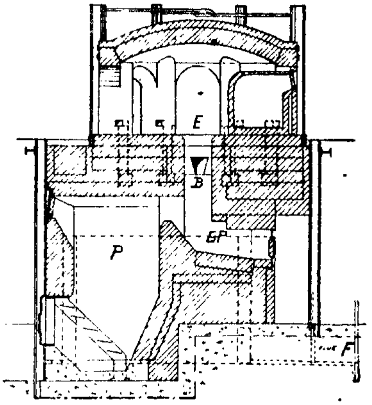


FIG. 1.

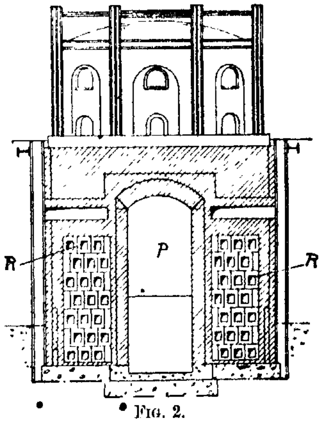


FIG. 2.

The pots. These are made in various sizes and shapes, and may be covered or open. Fig 3 shows different types: (*a*) a closed or covered pot is used generally for the highest grades of glassmaking. In one type, the 'oval' or 'doghouse' pot, the distance from the mouth to the back is considerably greater than between the side walls; (*b*) an open pot, used for medium quality glass, including plate glass and also, in America, for optical glass; (*c*) a skittle pot, used in the furnace in an inclined position so that the workman can readily gather the glass; (*d*) a potette, used occasionally in tank furnaces where the charging has to be done at the sides and not at the end of the tank, and also where the temperature at the working end makes the glass too fluid. The glass from the tank flows into the potette through an opening near the bottom. The pots are made of fireclay which has been carefully picked and weathered. Three fireclay constituents go to form the tempered mixture from which the pot is built, namely, a plastic clay called a bind clay, a base clay which should be as refractory as possible, and grog, or mixed fireclay which has been previously burnt to a high temperature. Analyses of fireclays which have found considerable use for glass pots are as follows: –

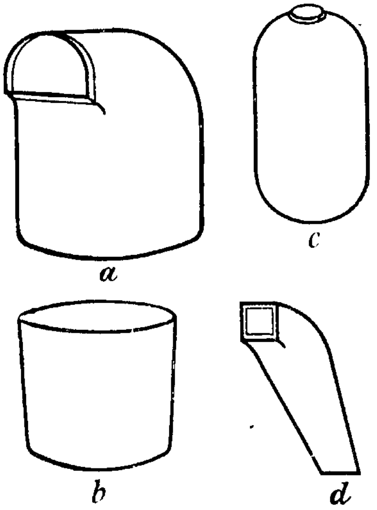


Fig. 3.

Percentage Composition of Clays after Ignition.

	1	2	3	4
SiO_2 . .	68·58	57·35	75·60	71·90
Al_2O_3 .	25·21	37·27	19·26	22·54
Fe_2O_3 .	2·52	2·19	2·30	2·59
TiO_2 . .	1·75	1·20	1·27	1·17
CaO . .	0·33	0·48	0·13	0·17
MgO . .	0·28	0·45	0·40	0·49
K_2O . .	0·96	0·42	0·89	0·72
Na_2O . .	0·37	0·67	0·16	0·42

1 and 2, Stourbridge clays; 3, Halifax, Yorks; 4, Huddersfield.

The chemical composition, however, is by no means a sure guide to the properties of the clay.

The relative proportions of clay and grog for a pot mixture vary. The following are some which have been employed: (1) Stourbridge base clay, 5; Stourbridge bind clay, 4; burnt mixed clay, 2; potsherds, 1½. (2) Mixed Stourbridge clay, 9; burnt Stourbridge clay, 5; potsherds, 5.

The proportions are always measured by volume. The first formula is typical of British practice, the second is one used in Germany. Potsherds are obtained from old pots by chipping off all glass and crushing to a regular grain size.

From the moist and plastic, tempered clay, the pot is usually built up by hand in stages, allowing intervals for the uniform drying of the mass, the base being considerably thicker than the upper portions. Pots are built quicker by using a wooden mould or shape, in which the clay is built and hammered to remove air bubbles. More recently, the casting process has come into use. The clay mixture is made fluid or converted into 'slip' by the addition of a small amount of a weak solution of sodium carbonate and silicate. This slip is poured into a plaster mould containing a core, and the plaster absorbs the moisture producing a firm structure. The crown or cover is usually cast separately, and united while both it and the body are still moist though firm.

The pot is now allowed to dry slowly, devices being employed in modern plants to control the degree of humidity. Subsequently, the pot is stored for months in a dry room at about 65°F. prior to use and kept free from vibration. In preparation for the glass furnace it is first heated in a special furnace called a pot arch, in which the temperature can slowly be raised to about 1100°C. or 1200°C., and the moisture, combined water and carbonaceous matter, driven off. In America, the following rate of heating is considered good practice: in 1 day, 75°C.; 2 days, 120°C.; 3 days, 371°C.; 4 days, 596°C.; 5 days, 816°C.; 6 days, 1025°C.; and 7 days, 1160°C. At the last-mentioned temperature the pot should be maintained for 30 hours.

The process of 'pot setting' next follows. The pot is removed from the pot arch on a heavy iron carriage and placed carefully in position in one of the arches of the furnace, and the front of the arch closed as rapidly as possible, preferably by fireclay blocks made to fit the arch. The only part exposed is the neck or mouth of the closed pot, and into this neck or mouth a flat slab or stopper is placed. An open pot stands entirely behind the furnace wall, being worked through an opening in the latter. When in position the pot should be allowed to remain empty for a day at as high a temperature as possible, short of incipient softening, before being glazed and filled.

Tank furnaces. These are of much later introduction than the pot furnace. Essentially they consist of a tank, the bottom and sides of which are composed of suitable refractory blocks, usually pot clay, a silica brick crown, and means of introducing batch and flame, and of removing glass. In size they may vary from a dead weight capacity of about 2 tons to 1250 tons, the latter being the approximate capacity of one window glass tank in America. Furnaces of from 100 to 350 tons deadweight capacity are quite usual.

Fig. 4 represents the cross-section of a glass tank furnace. It will be seen to be similar, generally, to an open hearth steel furnace, The bottom (A) consists of clay blocks supported on girders, resting on piers so that air has direct access to keep the bottom cool. The sides below the port mouth usually consist of three courses of fireclay blocks (B), in modern furnaces 9 inches thick. Round the mouth of the port (P) the blocks are of silica, and the crown (C) is of silica brick. The tank furnace shown is heated by producer gas and is of the regenerative type, the outer and larger chamber for preheating the air, the other the gas. In the furnace shown, the tongue in the port is air-cooled by two flues which run through it. The gas and air mix before entering the tank itself. A glass tank furnace always consists of a melting end and of a working end, and almost always there is a division between them. This often consists of a double wall of fireclay blocks with a square or a circular channel called the 'dog hole' communicating between the two portions. In other cases a floating fireclay bridge or dam consisting of two or three portions is used. In both cases the object is to prevent unmelted batch or other floating impurities from passing into the working end, where clear, bubble-free glass is required. The small rectangle (D) in the middle of the figure is the 'dog hole.' The larger rectangle in broken outline (E) corresponds to the end of the dog house, that is, a well which is merely an extension of the melting end of the furnace into which the batch mixture is charged.

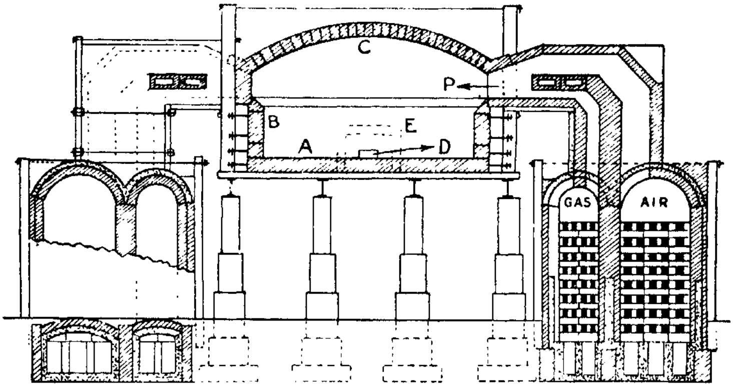


FIG. 4.

In modern furnaces the melting end only has gas ports, and these may be from two to seven or more in number, depending on the size of the furnace. Reversal of the direction of the flame takes place at least each half-hour.

The fusion process. In a pot furnace, supposing the pot to have been set and maintained for some time at the temperature of the furnace, a small quantity of cullet is usually added so as to furnish a glaze for the sides and bottom. Batch is then filled in by hand (except in some plate glass factories where a changing machine is used) and melting begins. Gas is given off from the batch materials, mainly carbon dioxide and moisture, and helps to stir up the molten mass. When all batch material has disappeared, bubbles of gas usually remain, and to eliminate them the temperature is allowed to rise, thereby reducing the viscosity of the glass and enabling them to escape. Assistance is sometimes necessary in this 'fining' or 'plaining' process, as it is called, and is given by pushing small pellets of ammonium nitrate or white arsenic as far below the surface as possible, or by water, pushed to the bottom in a blowpipe. These materials produce large bubbles on volatilisation and sweep out the small ones. When free from bubbles the glass is ready for working after it has been sufficiently cooled as to attain the workable consistency, and after skimming the surface from impurities.

In a tank furnace the charging in of batch and the working of the 'fined' glass are continuous, as previously explained, and the temperature is maintained constantly higher at the melting than at the working end.

THE MANUFACTURE OF DIFFERENT TYPES OF GLASSWARE.

The manipulation of glass and its formation into articles of glassware can be carried out entirely by hand, in many cases now also by machine. Machinery is now rapidly displacing hand labour for the common types of glassware capable of being produced in bulk to a standard pattern. In practically all cases the molten glass in the furnace is taken and shaped straightway into the articles required. Two exceptional cases are: (1) in the manufacture of better-class optical glass lenses and prisms, where the pot of glass is allowed to cool down slowly and the cold pieces of glass form the basis of further working; (2) in the lampworking or bench-glass blowing industry, the raw material for which consists of glass tubing or rod previously made at the furnace.

Manipulation by hand. The processes involved and tools used are numerous; two or three of them are common to almost every operation, some others are also of very general use. Thus, gathering glass on a blowpipe and marvering it or shaping it in a shaping block are the usual initial stages in making any glass object.

Fig. 5 depicts several of the more essential tools. The blowpipe (*a*) has a rounded end for mouth-piece and a 'nose,' usually slightly trumpet-shaped on the end of which glass is gathered by dipping into and rotating in the molten glass. The marver is a polished iron plate on which the gathered mass is rolled on the end of the marver until it attains a cylindrical form, called the *parison*, either hollow or solid, the hollow form being obtained by blowing down the pipe. The glassmaker's chair (*b*) has projecting arms on which the blowpipe is rolled backwards and forwards in order that the spinning or rotating shall preserve the rounded outline of the vessel. At this chair sits the master workman, or glassmaker, who finishes the article by means of various tools, such as the tongs, shears, callipers, and flattening boards shown in Fig. 5, in conjunction with rotation of the pipe.

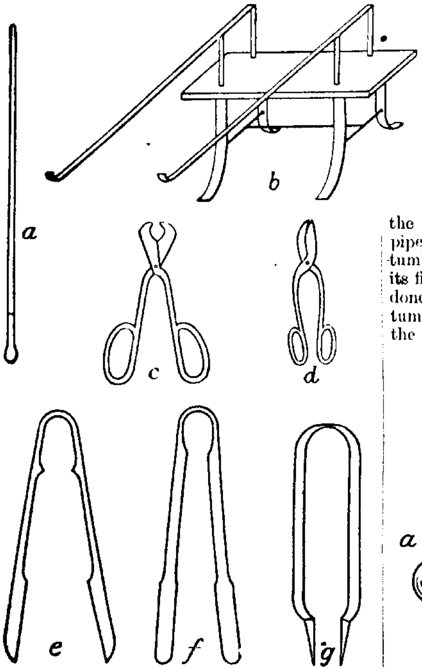


Fig. 5.

The various types of hand operation may be classified as (1) free hand work, involving gathering, marvering, blowing, and drawing as in making glass tubing; (2) turned work, or chair work, involving, may be, all the preceding processes together with the use of tools; (3) mould blown work, in which the marvered gathering is blown out in a mould—bottles, electric lamp bulbs, beakers, and flasks; (4) combined mould and turned work. This last is now common. Nowadays the bowl of a wine glass is frequently blown in a mould and the stem and foot added at the chair.

The following diagrams (Fig. 6) will serve to illustrate the operation of producing the hand-made tumbler, that is, an example of turned work. A very small quantity of glass is gathered on the end of the blowpipe and blown out into a small bulb (*a*). This in turn serves as the centre round which a further gathering (*b*) is made, sufficient for the size of tumbler to be made. By blowing down the pipe and also rotating the mass of glass in a shaping block, the shape (*c*) is obtained, the constriction being made so that eventually the fully blown vessels can be detached readily. By swinging the iron slightly, and by the further use of the shaping block, the parison is given a slightly conical shape (*d*), after which, by blowing and swinging, shape (*e*) is obtained, and finally (*f*), after the somewhat thicker bottom has been flattened out by contact with a flat and perfectly smooth iron plate. The pipe is detached by drawing a tool across the constricted part of the shoulder while the vessel is still hot and then giving the pipe a slight tap at its extreme end. The tumbler, with adhering shoulder, is now given its final form in one of two ways. This may be done at the chair by placing the bottom of the tumbler in a holder, reheating the shoulder in the mouth of the furnace, and cutting it away by means of shears. The glassmaker then finally rotates the cylinder on the arms of the chair, and by means of tongs rounds off the lip. The second process of finishing consists of making a scratch horizontally on the tumbler, at the required shoulder height, and then causing a crack to follow this scratch by rotating the tumbler at the top of the flame from several fine-pointed gas jets. Cracking off machines

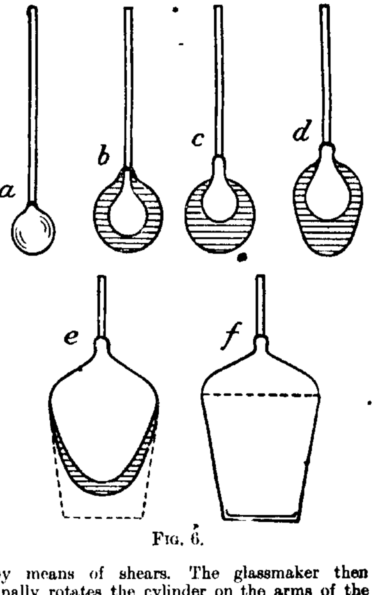


Fig. 6.

are constructed in which these processes can be readily carried out. The edges are rounded off by gas flames, applied either in another portion of the cracking off machine, or, by placing the tumbler in a holder and rotating the mouth in a gas flame.

In the case of mould-blown glassware, the gathering of glass after being marvered and formed into the parison, is blown out into a mould corresponding to the external size of the article required. The moulds may be of wood, carbon, brass, or iron. Moulds of special alloys have also been tried. The moulds of wood and carbon produce the best finish, whilst the iron moulds are less satisfactory from this point of view, although their durability causes them to be used in the majority of cases. Metal moulds may be used dry or may be covered with some form of lubrication, usually a paste, in which case the moulds are referred to as paste moulds. The paste is frequently a mixture of finely-divided carbon, such as lamp black, red lead, and linseed oil, but other forms of paste are in use. The paste must be thinly and uniformly spread, and the moulds after each blowing operation are dipped into water to cool them and prevent the paste being burned away too rapidly. Electric lamp bulbs, chimneys, blown tumblers, beakers, and flasks are blown in paste moulds.

Hand-made bottles are almost invariably blown in dry moulds. The process involves gathering at the end of the pipe, marvering into the parison, which usually has a somewhat smaller diameter at the end adjacent to the pipe than at the free end, swinging slightly to cause elongation, and then blowing out into the mould. Two methods of finishing the bottle are used according to the thickness of the neck. In heavy bottles with a thickened neck the latter is made at the furnace by the bottle maker, who adds an additional ribbon to the neck where it has been broken off from the pipe, and then by rotating the bottle at the chair and inserting a neck-forming tool the neck is given its final shape. In lighter made bottles, such as those used for medicines, the end which has been burst off from the blowing iron, is softened in a small subsidiary furnace known as a glory hole, usually heated by town gas or oil, and the neck is formed by pressing back the softened portion of the glass by means of the neck-forming tool.

GLASSMAKING MACHINES.

These are of various types. Six main types may be distinguished according to the process involved.

1. *Pressing machines*, as used for thick and heavy dishes, glass reflectors, jars, &c.

The machine may be hand operated, as in the case of large glass dishes. The mould consists essentially of two parts, namely, the mould proper into which any design may be cut so as to produce the design on the exterior of the glass article, and the plunger, corresponding to the interior of the vessel. The mould is fed with the requisite quantity of glass, and the plunger brought vertically down into the middle of the mass of glass, pressing it out so that it occupies the mould completely.

2. *Blowing machines*, either semi-automatic or fully automatic, in which the gathering of glass is blown out into a mould. Such machines are used for making glass chimneys, blown tumblers, electric light bulbs, &c. The manufacture of the latter is referred to later.

3. *Pressing and blowing machines*. In such machines there are two sets of moulds. The first into which the requisite quantity of glass is charged is called the 'parison mould.' This gives the initial shape to the neck of the vessel, the neck being formed by a plunger under pressure, in some cases by suction. The second set of moulds, known as 'finishing moulds,' have the glass from the parison mould transferred to them and the article then blown up to its complete shape and size.

4. *Drawing machines* such as those in which sheet glass and also glass rod are drawn out continuously.

5. *Blowing and drawing machines*, such as for the continuous manufacture of glass tubing and cylinders for window glass.

6. *Casting and rolling machines*, as in the manufacture of plate glass with its various varieties of rolled, ribbed, and wired glass.

A few illustrations will now be given of the production of different types of articles in glass.

Considering these types in the order of the classification given previously, common forms of glass ware made from sodium-calcium glass come first.

Bottles. The hand process has already been referred to. It is now largely confined to small bottles such as are used for medicines and perfumes, and especially the small bottles which are to be provided with a ground-in stopper. Most bottles and jars are now made by machine.

Fig. 7 illustrates one modern type of bottle machine, namely, the O'Neill. The machine consists of two circular tables each carrying six moulds, the one table carrying the parison or neck-shaping moulds (P), and the other the finishing moulds (F), seen in various positions in the figure, one of them being open. Glass is fed into one of the parison moulds from the furnace, and after insertion the operator touches the trigger (T) by means of his blowpipe, when the machine is set into operation and the mould moves forward to its second station. At the second station a blowing head (H) descends on to the top of the parison moulds, and the plunger is forced up from below to form the neck. At the fourth station the parison is transferred to the second table into the open blow mould, which then closes round it, and a blowing head at the second station on this table comes down and blows out the bottle. A further automatic device removes the bottle from the mould. When fed by hand such machines make from 10 to 15 bottles per minute according to size.

Machines of this type are also adapted, by using suitable moulds, for producing jars and lamp-shades.

The machines may be made fully automatic by feeding them either by means of what is known as a flowing device or by a glass feeding device. In very recent years these devices have come into extensive operation. In all cases the device is attached to a glass tank furnace; pots are unsuitable. Usually it consists of a short trough, constituting an extension of the tank furnace, and from the trough glass either flows by gravity or is propelled mechanically through an orifice, below which a pair of shears severs the glass into pieces of uniform weight. In the Hartford-Fairmont feeder, the temperature of the glass in the trough or fore-hearth is controlled by gas burners, and the glass is scooped over a spout at the end of the trough by means of a paddle. The operation of the feeding device is timed so as to correspond precisely with the motion of the glassmaking machine, so that a mould stands ready below the feeder at the moment when a piece of glass is severed by the shears.

Machines similar to the O'Neill are the W. J. Miller, the Lynch, the Edward Miller, the Teeple, the Cox, and the Hartford-Fairmont, all of them of American design.

Fig. 8 illustrates the 15-arm Owens machine, which is completely automatic. Each of the arms is provided with a parison mould and a finishing mould. In operation, the parison moulds as they are carried round the machine are, by a special movement, lowered into a revolving circular trough of glass fed from the main melting tank furnace. Glass is sucked up into the parison mould and the neck is formed by suction, and not by pressure in this case. As the parison mould leaves the trough a knife severs the excess glass from the bottom of the mould. The parison is next transferred to the finishing mould and blown out completely.

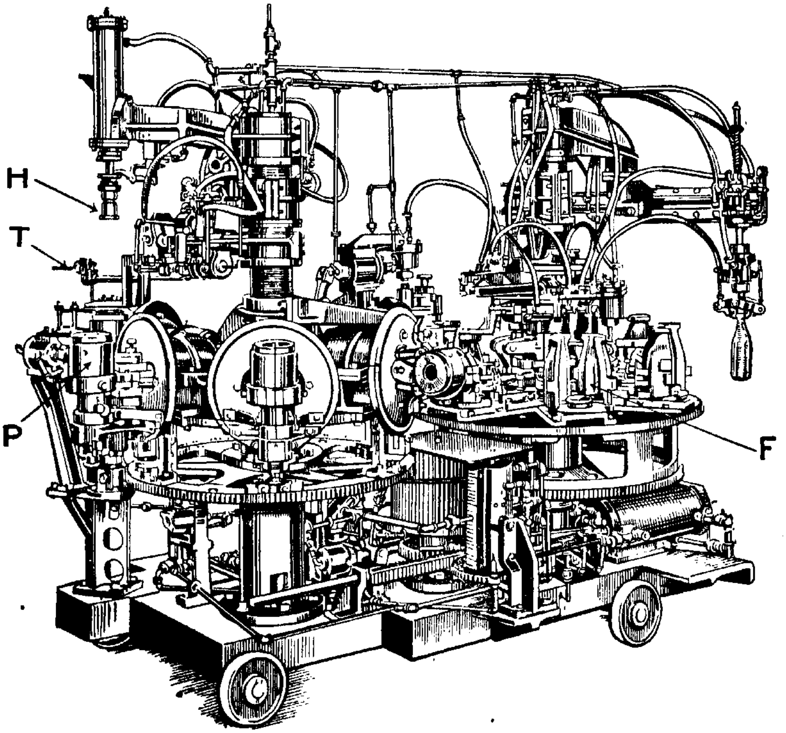


FIG. 7.

Such machines have actually been adapted for making bottles and jars of all sizes, from about ⅛ oz. up to a carboy holding 15 gallons. In the case of very tiny bottles as many as 160–200 per minute are produced. This quantity is obtained by making each mould double or triple, so that at each rotation either 30 or 45 bottles are produced.

Window glass. Window glass is made by hand and by various types of machines. In the hand process the figures (Fig. 9, p. 396) illustrate the several stages of the operation. Glass is gathered and marvered, and shaped into the ball (*a*). By rotation and blowing in a shaping block, the pear shape (*b*) is attained, and subsequently (*c*) and (*d*). The glass is then swung, pendulum fashion, at the end of the blowpipe in a rectangular pit, the operator standing on a platform. The end of the cylinder may have to be reheated several times in the mouth of the furnace before the full length is attained. The end of the cylinder is cut open with the shears, and by rapid rotation the mouth so formed expands until of the same diameter as the main portion (*g*). The shoulder is then cracked off (*h*). The size of the cylinder made varies in different countries. A length of about 5 feet 6 inches and diameter about 12 inches is frequent in this country.

Much larger cylinders are made by machine. In one process a charge of about 550 lbs. of glass is removed from the tank furnace in a ladle, transferred to a shallow circular fireclay trough, and after its temperature has been adjusted by gas flames, a blowing head is lowered into the glass, kept there until the glass adheres, and is then drawn out slowly, air under low pressure (1–2-inch water pressure) passing down the stem and blowing out the glass which assumes and retains the cylindrical form as the head is raised. Heavy cylinders between 300–400 inches long and 26 inches or more in diameter can be drawn.

The cylinder is cut into lengths by an electrically heated wire, and each portion split longitudinally by a red-hot iron rod (*k*). In some cases the cylinder is split into two parts. The split lengths (*l*) are placed in a flattening furnace on a smooth stone table and flattened by use of a wooden block.

When flat, it is passed forward, after slight cooling, into the annealing kiln.

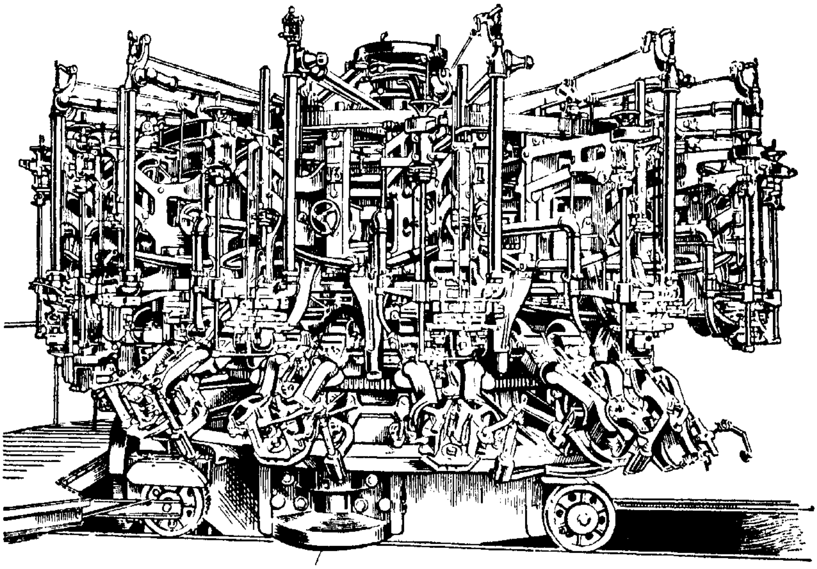


FIG. 8.

Two processes of window glass making by machinery produce the flattened sheet straightway. These are the Fourcault and the Colburn processes respectively, the latter being better known as the Libbey-Owens process. In the former, a bait which may be of metal, or a strip of glass, is let down into a well which forms the extension of a tank furnace. The adhering glass is then drawn vertically upwards, and at a short space above the well passes between rollers which not only assist the upward movement, but keep the sheet flat. The long chamber up which the sheet is drawn also serves as the annealing chamber. In the Colburn or Libbey-Owens process glass flows from a tank furnace into a shallow trough into which a metal bait is lowered. The bait with the adhering glass is then drawn upwards, vertically, for a distance of about 3 feet, and then is passed over a metal roller into the horizontal position, and on to a travelling belt. The glass sheet is thus conveyed horizontally through an annealing oven a distance of about 200 feet. The drawing operation is carried on at a rate varying from about 26 to 72 inches per minute, according to the thickness of the glass required.

Plate glass is made on a long iron table which can be traversed by a heavy iron roller. The table is spread with a layer of sand to prevent the glass sticking, and for the same purpose the roller is scored in such a way that it has a somewhat roughened surface. The glass is melted in open pots and poured evenly before the roller, which is then moved forward along the table. Immediately after being rolled the piece of plate is transferred to a very long lehr, or annealing oven, which may exceed 300 feet in length, where it is cooled down. It is then cut up into suitable pieces and fixed, in plaster of Paris, on a circular grinding table and ground down with water and several gradings of sand, commencing with the coarse and ending with the finer gradings. Emery may subsequently also be used. After the grinding of both sides, the pieces are re-embedded in the table and polished by means of water and rouge.

Strengthened sheet glass, for constructional work, is made in several different ways. Wire glass is one important form of such glass. In the latest method it is formed by crimping the wire mesh, placing it on the casting table, pouring glass over it and rolling out the sheet in the ordinary manner.

A more recent type of strengthened glass has been produced by rolling a sheet of celluloid as a layer between two sheets of plate glass of half the usual thickness, and in another type both wire and celluloid are embedded.

Triplex glass, which rendered very great service during the war in motor cars, aeroplanes, and submarines owing to its non-shattering properties when fractured, is produced by cementing together three sheets of glass so closely as to appear one. On being struck by a missile such as a bullet, cracks radiate in star form from the point of contact, but no splintering occurs.

Lead-containing glasses are used very largely for table-ware and general artistic glass. The manipulative process is almost always that of hand operation along the lines previously indicated.

Electric lamp bulbs are made by hand and by machinery, in both cases by blowing into paste moulds.

Two types of machines have recently come into use, the one known as the Empire machine, being semi-automatic, the other, the Westlake, being fully automatic. In the former, the glass is gathered by the workman at the end of a blowing iron, and the blowing iron then inserted in the machine where the glass is marvered and finally blown out into the mould. The machine has four arms. The Westlake machine is fully automatic, and may have 12 or 24 arms. Glass is gathered by an arm which is projected into the glass furnace and transfers the glass obtained into a cup, and thence to the end of a blowpipe, which is, initially, in the vertical position with its nose upwards. The arms carry out the various operations similarly to the human blower, but the productive capacity is very much greater, a 12-arm machine producing at least 1000 bulbs per hour.

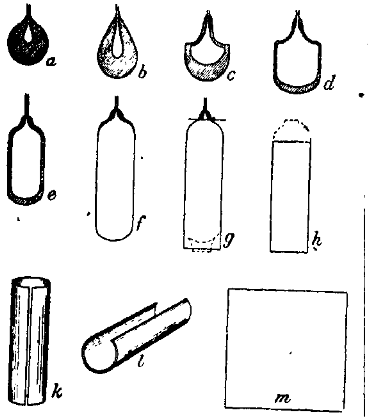


FIG. 9.

Chemical, scientific, and heat-resisting glassware. Almost all types of this particular class are made by hand. Flasks and beakers are blown in paste moulds. Fig. 10 shows a mould for a flask, and Fig. 11 the initial form of a beaker. The shoulder is then cut off by the second process described in connection with the tumbler (p. 392), and the edges are heated and flanged and a lip added where desired.

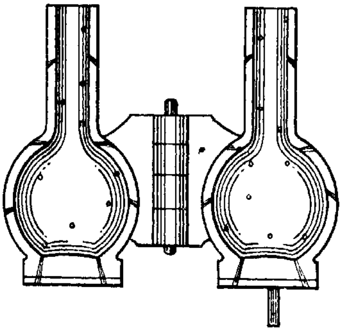


FIG. 10.

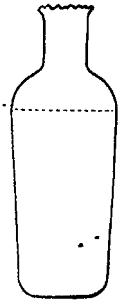


FIG. 11.

Glass tubing is drawn by first marvering a thick hollow cylinder of glass, built up by several gatherings, and then lowering this cylinder in a vertical position until its base unites with a disc of hot and soft glass, attached to a holder held by another operator. When the union is firm, the assistant with the holder walks backwards along a wooden track crossed by strips of wood, pulling out the glass tubing as he walks, the chief glass blower at the same time turning his blowpipe round and round and occasionally blowing down it to prevent the walls of the glass from collapsing. The tubing is laid on the wooden strips and after cooling cut into lengths.

The Libbey-Owens machine, invented by Danner, improves the uniformity and enormously increases the production of glass tubing. Glass from a furnace flows in a stream on to an inclined rotating clay tube slightly cone-shaped, and runs down to the end (Fig. 12). It is prevented from forming a solid mass by a current of air transmitted by an iron water-cooled tube enclosed by the clay tube. The glass pulled from the end of the latter is hollow and cylindrical. The pulling is done by a machine, attached to which is a wheel which cuts the tubing into lengths. Glass tubing can by this machine be made at more than 120 feet per minute. When glass rod is required, the air current is shut off.

Optical glass. Since the use of decolorisers in glass results in a loss of transmission of light, it is essential that practically iron-free materials be used, and that the pot be as little subject to corrosion as possible.

After the batch has been melted, a water-cooled fireclay stirrer is inserted in the pot and the glass stirred thoroughly so as to remove both bubbles and layers of different density. In one works, stirring is actually begun during the melting. After the glass is 'plain' the stirring is continued while the temperature is being reduced, until the glass is too stiff for further movement.

The pot is then allowed to cool very slowly, either by bricking up the furnace, if the latter is of the unit type, or transferring to a heated pot arch, where the temperature is slowly reduced, or again, by removing the pot and covering with a non-conducting cover.

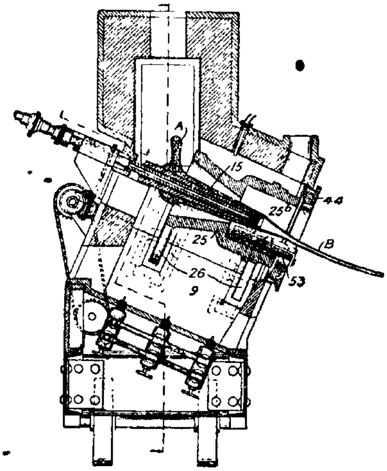


Fig. 12.

When cold, the glass is found to be broken up into angular portions. Usually most of the glass must be rejected because of the contamination derived from the pot. Often, only about 20 p.c. is recovered as slabs of good glass.

For use, the angular portions are re-heated in a muffle furnace to softening point, then pressed into rectangular slabs and subsequently annealed. Fine annealing, for the removal of all strain, may take from two to three weeks.

The slabs are cut across, and opposite ends polished and examined in the polariscope for striæ and strain, as also for bubble.

The Annealing of Glass.

All articles of glassware, as also slabs of optical glass after being made into regular block form, need to be annealed in order to remove strain set up in them during the cooling process. Glass, being a very viscous material, and having only poor conductivity, sets hard on the exterior, while the mass in the interior is at a distinctly higher temperature and is more fluid. Consequently, stresses are set up on the exterior and strain on the inner layers, so that these inner layers tend to contract on to the outer ones. Where the exterior is chilled rapidly, as in the production of Rupert's drops, by allowing small blobs of molten glass to fall into water, the interior layers contract on to the exterior to such an extent as to leave an apparent bubble. The stress and strain in glass can be removed as soon as the glass is sufficiently soft. If the glass is quite soft then the strain is relieved rapidly; or, in other words, annealing takes place quickly. If, on the other hand, the glass is only slightly removed from the rigid state, then annealing requires a considerable period of time. In practice, speed is an important factor in the production of most articles of glassware. In such case the articles are heated up to a temperature as high as possible, just short of deformation, so that the strain is rapidly removed. The annealing temperature employed under these conditions has been defined as the upper critical annealing temperature. The glass must subsequently be cooled down at a fairly slow and definite rate, until it has become so rigid that movement of different layers is practically impossible, so that no strain can be reintroduced. The temperature of sufficient rigidity has been described as the lower critical annealing temperature. In the case of optical glass it may be advisable to anneal at a temperature only slightly exceeding the lower critical annealing temperature. A slight reduction of temperature, which can be made very readily, is then sufficient to remove the glass from the region of possible recurring strain.

The actual upper annealing temperature and also the length of range between that and the lower value, obviously depend on the viscosity of the glass and on the rate of change of viscosity. These in turn depend on the composition of the glass.

The oxide constituents which tend to reduce the annealing temperature are sodium oxide, potassium oxide, and lead oxide. Lead-containing glasses can be readily annealed. English crystal glassware has an upper annealing temperature in the neighbourhood of 450°C., and most commercial types of lead glass are readily annealed at temperatures of 450°C. to 500°C. Window glass, and, generally speaking, sodium-calcium glasses, have an annealing temperature round about 550°–560°, although, according to the composition and the percentage of calcium oxide, the value may range from 540° to 610°. Miner's lamp glass which contains high silica and boric oxide content requires a temperature of approximately 590°, whilst resistance glass for chemical apparatus may need a temperature as high as 630° (English and Turner, J. Soc. Glass Tech. 1918, 2, 90; 1919, 3, 125 and 278; 1920, 4, 387).

In commercial practice two main types of furnace are used for annealing, namely, the kiln and the continuous annealing oven, called the 'lehr.'

The use of kilns is now almost entirely confined to heavy glassware for table use, and similar articles on which work such as cutting and engraving has subsequently to be done. In America gas-fired muffle kilns are used for thick glass jugs, tumblers, &c., with much advantage.

The continuous annealing oven, or lehr, consists essentially of a brickwork combustion chamber extending about 10 or 12 feet from front to back, and leading into a continuous tunnel, so that the total length from the front of the combustion chamber to the end of the lehr may be from 40 to 70 feet long, and in the case of window and plate glass very much longer, even exceeding 300 feet. The combustion chamber is usually heated by gas, although oil and coke heating are still used, and in this section of the lehr the object aimed at is to maintain the articles at the required annealing temperature so that all strain is removed. The heated air and, except where the combustion chamber takes the form of a muffle, as in the modern "muffle lehrs," the products of combustion may pass down the tunnel for a certain distance which can be controlled by flues and dampers. The width of the lehr is frequently about 6 feet, but may be as much as 12. The articles of glass-ware may be placed in pans which are linked on to one another and drawn through the lehr gradually, on pulleys attached to a fixed track. In a few cases the articles are placed in wagons which run on a track. In modern lehrs for mass production an endless belt carries a moving platform on which the articles are placed, and the speed of this platform is controlled mechanically according to the character of the glass and the time required for annealing.

The best test of satisfactory annealing is to examine the articles of glassware between crossed Nicols. A well-annealed specimen permits practically no light to pass through it, whilst a strained sample will transmit an amount of light dependent on the degree of strain.

Hardening of glass. This may be carried out either by the process of De la Bastie or by that of Siemens. In the former, discovered in 1873, the glass article, while still red hot, is quenched in a bath of oil or fat, the actual temperature of both glass and the bath, that is, the quenching range, depending both on the composition and thickness of the glass. Sodium-calcium glasses can withstand a greater quenching range than the lead glasses. The process results in the sudden chilling of the outer before the inner layers, so that the surface layers undergo greater shrinkage, causing them to be subjected to compression, whilst the inner layers, on the other hand, are in tension. Glass in this condition becomes less brittle, is more elastic, and capable of withstanding mechanical shock and sudden change of temperature, but if the surface is once broken the whole mass becomes shattered.

In Siemens' process, the temperature of pressed glass articles is rapidly but uniformly reduced in special moulds, or between metallic or clay plates maintained at a suitable temperature. Pavement lights treated in this manner resist cutting by a diamond.

Compound glass, the basis of the durax water-gauge tubes, was developed by Schott to give the same resistance to shock and change of temperature as hardened glass. A gathering of glass 16 (III) is made over 59 (III) and the cylinder drawn into tubing. The former has the larger thermal expansion (and contraction), so that on cooling the outer layer is under compression and the inner under tension. When the tubing is heated up both compression and tension become relaxed. Glass 59 (III) which forms the inner layer is also very resistant to the action of water and steam.

THE DECORATION AND AFTER-TREATMENT OF GLASS.

The processes by which glass may be ornamented or marked are numerous. They may be divided into two classes, namely: (1) those carried out at the furnace during the formation of the article; (2) those dependent on the treatment of the surface. To the former belong such processes as casing, spinning, filigree, and mosaic working. The second class is divisible into two groups, according as the surface is treated by mechanical means, such as those involved in decoration by grinding, cutting, bevelling, polishing, engraving, sand-blasting, and frosting; or by the action of chemical reagents, such as in etching, silvering, iridising, and in glass painting. In rather a different category is the art of treating glass tubing or rod by lampworking or bench glass blowing.

Casing consists usually in spreading a uniform, thin layer of colour over an article of colourless glass. The coloured glasses most commonly used are ruby, blue, and opal. The essential conditions for casing are that the glasses shall have approximately equal coefficients of expansion and be soft or plastic. Glasses of fairly high lead content are very suitable for such treatment. One method of carrying out the operation is to make a gathering of the colourless glass, to blow it up slightly, and then dip into a pot of the coloured glass in such a way that a uniform outer layer is obtained. The combined gathering is then worked up by turning or blowing in the usual manner.

Banded glass, feather glass, filigree glass, and the insertion of an enamel backing in thermometer and other tubing are all special examples of casing. The enamel backing of tubing is a simple example. One method of making it consists in preparing a rod of opal glass and inserting a length of it in a vertical recess in a mould. The parison of colourless glass is introduced into the mould so as to come into contact with, and pick up the opal rod, after which the parison is marvered further to complete the union. A further gathering of colourless glass to cover the opal is then made and the whole mass drawn into tubing in the ordinary way.

For details of manipulative methods of decorating glassware at the furnace the reader should consult Hohlbaum's *Herstellung, Bearbeitung, und Verzierung des feineren Hohlglases*, 1911; Apsley Pellatt's *Curiosities of Glassmaking* contains a good account, but is unfortunately long out of print.

Cutting for decorative processes, largely employed for thick table-ware, is carried out in several stages. The pattern to be followed is marked out in chalk and then cut over by an edged iron wheel working in a vertical plane, the edge being constantly fed with sand and water. This first, or roughing process, leaves the cut portions with a roughened surface which is then gone over by a similar stone wheel, Craigleith stone being in common use, and finally by a wooden wheel using putty powder or other soft polishing material; or again, the final polishing stage may be carried out by immersion in an etching bath for a short period.

In some classes of pressed glassware the roughing process, or use of the iron wheel, is abolished by cutting the pattern in the mould so that the article receives the main impression at the furnace. Immediately after being pressed, the interior of such articles, usually dishes and bowls, is 'fire polished' by the action of a hot gas flame which removes all roughness caused by the plunger of the press. The article may be sold without further treatment, or the pattern on it may be considerably improved by the use of the stone wheel and the subsequent polishing process.

Engraving is carried out by sharp-edged or bevelled copper wheels varying in size from that of a pin's head to 2 inches or more in diameter, the spindle carrying the wheel being fixed in the chuck of a lathe. The glass article is held in the engraver's hands against the rotating wheel.

Very pleasing effects are obtained by cutting or engraving designs on cased glass, especially where the cutting penetrates the outer coloured layer to the inner colourless one.

Glass grinding is carried out not only for decorative purposes, as described under 'cutting,' but also in the production of lenses and prisms, glass stoppers, both solid and hollow, all-glass syringes, and in the smoothing off of various articles whose ends would otherwise have sharp edges through being cracked off in a flame, articles such as blown tumblers, chimneys, and miners' lamp glasses. Lenses for grinding are embedded, a large number simultaneously, in pitch. The 'block' so produced may be flat if plane lenses are required or may have a curved surface corresponding to the lens curvature required. The grinding is done by a tool or head of iron with its surface shaped to the required curvature. In the grinding process this tool moves over the block of lenses in a path which is continuously varying. Fine carborundum or emery powder are the usual grinding media with water, and rouge follows in the polishing stage.

For the bottoms and edges of glass articles large carborundum wheels, revolving in the horizontal plane or carborundum cylinders with the flat-end set vertically, are used. In the former case, the articles to be ground are held vertically, in the latter, horizontally. In modern machines, a large number of articles, such as tumblers, can be treated in a very short time. Following such edge grinding, tumblers and similar articles are transferred to an 'edge melting' machine consisting of a continuous belt or track, by means of which the articles are carried through a zone of flame obtained from a double row of impinging gas-jets where the edges are rounded off. Solid glass stoppers are ground by fixing in a chuck on a lathe and grinding with sand and water to the required degree and taper.

The grinding of hollow stoppers and internal grinding generally is done by soft steel or iron drills, suitably tapered and fixed in the chuck of the lathe. The rotating drill is inserted in the article and fed with water and one of the various grinding powders, which include diamond dust.

Sandblasting, employing the cutting action of wind-driven sand grains, was introduced by Tilghmann in America. The matt surface so produced can be controlled in extent and design by covering part of the glass surface. For this purpose a metal stencil may be employed, or a transfer comprising some definite design done in oil or fat or other soft material which prevents the cutting action of the sand, and can subsequently readily be removed, leaving a pattern or design in clear glass.

Frosted glass, in which the surface is marked in fern-like patterns, is based on the discovery of Cailletet (Compt. rend. 1902, 134, 400), who found that a coating of glue or of gelatine, containing some neutral salt, when applied to glass exerted so powerful a disruptive action during its drying and shrinkage as to produce frost-like patterns when the dried coating was removed. The process is applied to window glass. One mixture employed consists of gum sandarac 18 parts, gum mastic 4, benzene 40, ether 200 and the mixture is poured uniformly over the previously cleaned surface. The sheets of glass after treatment remain in a drying room until the gelatine is set, and afterwards in a warm room to speed up the contraction of the coating.

Etching, by means of hydrofluoric acid or fluoride solutions, is commonly employed both for decorative purposes and for marking graduated glass instruments. The reaction may be expressed by the equation:

$$K_2O,CaO,6SiO_2+28HF=2KF+CaF_2+6SiF_4+14H_2O.$$

The effect produced depends on the type of glass, and on the nature and strength of the etching solution. The glasses of high lead content, as used largely for table ware, are best suited for etching. Hard potash glasses and chemical resistance glass are only very slowly attacked. Dependent on the solution, one may obtain matt etching, clear etching, or may even get a polished surface. A good matt etching is obtained by immersion at ordinary temperature in a solution of 10 parts HF in 100 water, the solution being neutralised by potassium carbonate and 2 additional parts of HF then added. Aqueous solutions of ammonium fluoride, usually made as required by neutralising the acid with ammonium carbonate, act rather slowly. A mixture of ammonium fluoride 5 parts, hydrofluoric acid 2, and water 5, will produce at ordinary temperature a very rough matt etch. A satin etch is obtained by a solution of potassium fluoride 10, hydrochloric acid 1, water 100, the temperature of the solution being 40°-60°C. For line etching, used either for simple lines as on graduated instruments, and the simple line decoration on tumblers, or for etched designs as a substitute for engraving, dilute HF is used, a suitable solution for deep etching being hydrofluoric acid 1, sulphuric acid 1, water 4–5.

Acid polishing may be carried out by hydrofluoric acid in the presence of strong sulphuric, the liquid being agitated to prevent the deposition of fluorides which normally produce the matt surface effect.

If a line design is to be etched, the glass surface must previously be coated with a resistant material, and the design then traced by an instrument with a fine point. Two such 'resists' are: (1) asphalt 5, resin 2, tallow 1, Venetian turpentine 2, turpentine 12; (2) asphalt 5, resin 3, Venetian turpentine 1, turpentine 8, beeswax 1·5.

Other designs may be applied by means of a 'transfer.' The latter is prepared by engraving the design on a copper plate, coating the latter with a 'resist,' and removing the excess so that only the cut design remains filled, then applying a piece of tissue paper to the design whereby a wax impression is transferred to the paper. The 'transfer' so produced is applied to the glass surface, the remainder of the latter not covered by the transfer being protected by a wax coating before the application of the etching agent, frequently used in paste form. After a few minutes the etching agent is washed off, leaving a matt surface design.

The markings on graduated instruments are usually rendered more clearly visible by rubbing into them finely-powdered barium sulphate, red lead, &c., or the introduction of a soft enamel.

Silvering for the production of mirrors was introduced in 1843 by Drayton to replace the tin amalgam method, but made a commercial success only through Liebig in 1867. The freshly-polished sheets of glass must be thoroughly cleansed previous to the application of the silvering solution, which is prepared from two essential solutions, one of silver nitrate, usually ammoniacal, the other an organic reducing agent, most often sugar. The rate of deposition depends on the temperature. Silvermann and Howe (J. Ind. Eng. Chem. 1917, 9, 1032) recommend for work at ordinary temperature, solutions of silver nitrate 0·636 gram made up with water to 100 c.c.; cane sugar, 34·2 grams dissolved in water, and made up to 100 c.c.; 80 p.c. methyl alcohol, and 0·8 p.c. formaldehyde solution. For the mixture, the volume used of the above four solutions are, respectively, 165, 10, 5, and 20. About 20 p.c. of the total silver content can be deposited in 40 minutes.

Copper deposits are usually made electrolytically on a previous coating of silver, the copper solution for electrolysis being of copper sulphate in Rochelle salt, made alkaline with caustic soda. By Chattaway's process (Proc. Roy. Soc. 1907, A, 80, 88) the deposition may be made direct. A clear solution is made by warming 1 part of freshly-distilled phenylhydrazine with 2 parts of water. To it, half its volume is added of a warm saturated solution of cupric hydroxide in strong ammonia. A hot solution of 10 p.c. potassium hydroxide is now added until a slight permanent precipitate is obtained. This liquid, when warmed in contact with a perfectly clean glass surface, gives a bright deposit of copper.

Aluminium deposits may be made on copper deposits by the metallic spraying process.

Iridescent glass, which in antique specimens is produced by surface decay, is artificially obtained by the action of metallic vapours. After being made at the furnace and while still red hot, therefore, the article is rotated rapidly inside an iron box or oven in which suitable metallic salts are volatilised. Various mixtures of salts are employed, such as: (1) stannous chloride 90 parts, strontium nitrate 5, barium chloride 5; (2) stannous chloride 90 parts, barium chloride 2, bismuth nitrate 5. The bright iridescent coating may be made matt by reheating several times in the mouth of the furnace. The iridescence may be greatly varied, as in Tiffany glass, by treating coloured glasses or those with patterns. Brilliant metallic effects may be obtained by adding a silver or a bismuth salt to the glass batch and reheating the object, before iridising, in a reducing flame whereby a metallic surface deposit is produced.

Glass painting is carried out by the various colouring oxides and compounds elsewhere described in this article. They are mixed with a suitable flux in which they may or may not dissolve. In the former case, when applied to glass, the painting is transparent, unless specially rendered opaque as by the addition of stannic oxide, whilst in the latter it is non-transparent. The flux for gold purple is obtained by melting a mixture of quartz 4 parts, red lead 3, borax 6; for other colours, a flux made from quartz 2, red lead 6–9, borax 1, may be employed. The colouring materials are both finely ground and thoroughly mixed, and the mixture may be used directly for painting, or it may first of all be sintered or fritted, and again finely powdered. In either case the fine powder is thoroughly ground with turpentine or other oil as medium, applied with a brush to the glass, and the latter then heated in a muffle oven to a temperature sufficient (about 800°C.) for the thorough fusion of the flux and colour to a brilliant surface. Slow cooling down is then desirable. The vitreous paints so applied should, for successful burning in, have a coefficient of expansion not greatly different from that of the glass treated.

Glass beads and artificial gems. Glass beads are made from previously drawn tubing of varying diameter and bore, and of various colours. The tubing is next cut into lengths suitable for the size of the bead. If the latter is to be cylindrical, the beads may be made at the lamp by merely softening the cut ends to round off the edges. For spherical beads, the cut lengths are kneaded in moist clay, or clay and ground charcoal, to prevent collapse of the walls during subsequent heating. The heating is carried out in a revolving drum, to redness, whereby the rounded shape is given and the edges melted.

The thin-walled spherical beads are made by blowing thin bulbs and either filling them with wax or coating them internally with 'essence of pearl,' consisting of ground fish scales in ammonium chloride. The second method produces the pearl beads. (For method of applying the pearl coating, *see* O. Parkert, Sprechsaal, 1919, 52, 23 and 191.)

Artificial gems are made by adding suitable colouring material to a glass with high lead content, and therefore of high refractive index and brilliance when cut. The colourless paste, or strass, may be made from sand 100 parts, red lead 150, potash 30, the materials being of high quality. The resulting glass may be ladled into water and subsequently re-melted to obtain homogeneity and then ground for admixture with the colouring agent. *Rubies* may be prepared from 1000 strass, 1 purple of Cassius, 5 stannous oxide, 10 antimony oxide; *emeralds* from 1000 strass, 1 green chromium oxide, 8 cupric oxide; *amethysts* 1000 strass, 8 manganese dioxide, 2 cobalt oxide. The strass and colouring matter must be thoroughly fused together and made homogeneous. Small porcelain pots holding up to 50 lbs. glass are used.

Quartz glass. Whilst ordinary glasses are produced by the fusion of basic oxides with silica, and in some cases boric oxide, it must be borne in mind that the use of such basic oxides is primarily to permit fusion to take place at the temperatures at present commercially attainable. Silica in itself possesses so many valuable properties that if it could be fused readily it would displace many types of glass. The high temperature of fusion restricts the scale on which melting can be carried out, but already, silica ware has become a recognised article of commerce, being worked into tubing, rod, beakers, flasks, crucibles, and other types of scientific apparatus, quartz threads for galvanometric mirror suspensions, nitric acid stills, sulphuric acid condensation plant, and chimneys for incandescent lamps.

Two types of fused silica ware are on the market, the transparent, made from quartz, and the opaque or translucent, produced from sand or crushed quartz. The *transparent* form is worked in the oxy-hydrogen flame, and the size of the article capable of being made is restricted to small crucibles and dishes, and the smaller sizes of flasks, beakers, and similar articles. The *non-transparent* silica can now be worked in masses up to 200 lbs. and tubes 4 inches or more in diameter form a stock article. The starting point for tubes is a hollow core of plastic silica produced by fusing a mass of white-sand round a central core electrically heated, the core being removed when the cylinder has been formed and drawn into tubing in the ordinary way. In the plastic condition such a silica cylinder can be drawn into lengths of 90 or 100 feet. The rough outer surface of the tube may be ground down and may be glazed, either electrically or by an oxy-hydrogen flame.

For articles other than tubing, the cylinder is closed at one end and blown in a mould by compressed air.

The temperature required for fusing and working the sand is 1800°C.-2000°C. As only a plastic and not a completely fused condition is reached, the fine air bubbles are not removed, and reflection from them gives rise to the silky, lustrous appearance characteristic of this type of fused silica. (*See* F. Bottomley, J. Soc. Chem. Ind. 1917, 36, 577.)

Quartz glass has an extremely small coefficient of linear thermal expansion, namely, $5{\cdot}2\times10^{-8}$, and articles made from it can be heated to redness and quenched in cold water without fracture. Hence its value for heat-resisting glassware. Unfortunately, fused silica ware cannot be maintained for any considerable period at temperatures higher than 1000°C. owing to its tendency to revert to the crystalline form stable at such temperature, namely, tridymite, when the article is liable to break down.

Fused silica is practically unacted on by water, and all acids except hydrofluoric acid and phosphoric acid above 400°C. It is, accordingly, of very great value in precise chemical analysis where water, neutral salt solutions, and acids are alone concerned. Further, as a consequence of its resistance to solubility by water, and its non-hygroscopic character, fused silica is a very good electrical insulator. As an acid material itself, it is naturally attacked by the alkalis, and the use of silica crucibles is therefore much restricted since metallic oxides cannot be fused in them.

Transparent quartz is transparent to ultraviolet light and on this account finds special use in the form of plates, lenses, and wedges or prisms in optical apparatus, and in mercury vapour lamps. The refractive index for the D-line is 1·45847, and the dispersion constant ν 67·92 (Gifford and Shenstone, Proc. Roy. Soc. 1904, 73, 201). W. E. S. T.

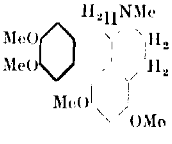
GLASS OF ANTIMONY *v. Antimony crocus*, art. ANTIMONY.

GLASS, TOUGHENED, *v.* GLASS.

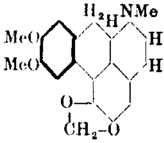
GLAUBER'S SALT. *Sodium sulphate* (*v.* SODIUM).

GLAUBERITE *v.* CALCIUM.

GLAUCINE $C_{21}H_{25}O_4N$ occurs in *Glaucium flavum* (Crantz) along with protopine (Battandier, Chem. Soc. Abstr. 1892, 62, i. 893). Crystallises in rhombic prisms, m.p. 119°-120°, $[\alpha]_D+113{\cdot}3°$ in alcohol, is a tertiary base and contains four ·OMe groups (Fischer, Arch. Pharm. 1901, 239, 426). It has been synthesised by Gadamer (*ibid.* 1911, 249, 680) and shown to be phenanthreno-*N*-methyltetrahydropapaverine, and therefore is closely related to dicentrine.



Glaucine.



Dicentrine.

Glaucine is tasteless and induces narcosis, accompanied by some tetanising action.

GLAUCONITE. (*Glauconie*, Fr.; *Glaukonit*, Ger.) Hydrated silicate of iron, potassium, &c., of variable composition, but approximating to the formula $KFe'''Si_2O_6.H_2O$, found as small rounded grains in sedimentary rocks. It was named in 1828, from γλαυκός, bluish-green, on account of its characteristic colour, which is of various shades of dark green. The typical occurrence of the mineral is the Greensand formation (below the Chalk) of the Cretaceous system, but it is also met with in sands, sandstones, marls, and limestones of all ages from the Cambrian, and is forming at the present day on the floor of the ocean. The granules measure about ¼ to 1 mm. in diameter. Under the microscope they show a clear green or yellowish-green, slightly pleochroic and birefringent material embedded in a network of black, optically isotropic, organic matter, the latter having the composition of humic acid. Since the glauconite material has the property of taking up dyes and of absorbing water, up to 30 p.c., from a moist atmosphere, it is probably colloidal, the optical birefringence being the result of strain set up by the network of organic matter. The mineral is decomposed by hot concentrated hydrochloric acid, and before the blowpipe it is fusible with difficulty to a black magnetic slag.

Analysis I is of grains isolated from a calcareous sandstone in the Upper Greensand at Woodburn, Carrickfergus, Co. Antrim (A. P. Hoskins, Geol. Mag. 1895). II from the Cambridge Greensand (G. D. Liveing, Geol. Mag. 1866). III gives the extreme values shown in ten analyses of glauconite grains isolated from

Eocene, Cretaceous, and Jurassic sandstones and from Lower Silurian limestone from various Russian localities; sp.gr. 2·40–2·87, varying like the colour—yellowish-green and dark green—with the percentage of iron (K. D. Glinka, 1896). IV, grains forming 83 p.c. of a sandy deposit dredged at a depth of 556 fathoms from the Pacific off Panama (W. A. Caspari, Proc. Roy. Soc. Edin. 1910, xxx, 364). V, similar material dredged at 110 fathoms from the Agulhas Bank, South Africa (W. A. Caspari, *loc. cit.*). Numerous analyses of glauconite are quoted by C. K. Leith, Mon. U.S. Geol. Survey, 1903, xliii. 240. Analyses of Swedish glauconites, by N. Sohlbom, Bull. Geol. Inst. Univ. Upsala, 1916, xv, 211.

	I.	II.	III.		IV.	V.
			Min.	Max.		
SiO_2 .	40·00	51·09	41·02	52·96	49·12	51·15
Al_2O_3 .	13·00	9·00	5·84	22·10	7·09	7·61
Fe_2O_3	16·81	—	8·17	23·43	25 95	18·83
FeO .	10·17	19·54	1·32	5 95	0·89	2·79
CaO .	1·97	0·30	—	8·37	—	—
MgO .	1·97	3·37	0·69	4 11	3 10	4·54
K_2O .	8·21	2·47	5·74	9·54	7·02	7·80
Na_2O .	2·16	3·56	0·30	0·98	—	—
H_2O .	6·19	10 80	4·45	7·88	7·12	7·56
	100·48	100·13	—	—	100·29	100 27

Closely allied to glauconite are the minerals celadonite (*v.* green-earth) and greenalite (*q.v.*).

The Greensand of England, consisting mainly of sandy beds with quartz grains, intermixed with glauconite, is developed in the Wealden area, the Isle of Wight, and extends from Berkshire and Oxfordshire to Norfolk and Lincolnshire. Some of the limonitic iron-ores of these districts may possibly, like those of the Lake Superior region, have been derived by the alteration of glauconite. The same formation has also a wide distribution on the Continent. In America, greensand and glauconitic marls of Cretaceous and Tertiary age are developed in New Jersey, Virginia, Kentucky, and Tennessee. The glauconite marls of New Jersey contain K_2O 1·54–7·08 p.c. with P_2O_5 0·19–6·87, and have been extensively used in the raw state as an agricultural dressing (*v.* Ann. Rep. State Geologist New Jersey, 1886, 1892, 1893). Those from Virginia have been used in the preparation of commercial fertilisers. Attempts have been made to extract potash from greensands (U.S. Geol. Survey, Min. Res for 1911, 1912, ii 901).

The frequent association of phosphatic nodules with glauconite deposits has some bearing on the origin of glauconite. The terrigenous deposits of green mud and sand formed on the floor of the ocean at depths of about 200 to 1000 fathoms, and found by the 'Challenger' Expedition to be of wide distribution, particularly off continental coast lines composed of igneous rocks, contain this mineral in considerable amount. The potash set free by the weathering of the felspars and micas of these rocks and carried into the sea is conserved by the formation of glauconite, but apparently only through organic agencies, which at the same time gave origin to the phosphatic nodules. Grains of glauconite are frequently found filling the chambers of foraminifera and other organisms; and in the artificial production of the mineral the presence of an organic acid seems to be essential (W. A. Caspari, *loc. cit.*).

L. J. S.

GLAZES *v.* FRITTS AND GLAZES; also POTTERY.

GLIADIN *v.* GLUTEN.

GLOBULINS *v.* PROTEINS.

GLONOIN. Syn. for nitroglycerin.

GLUCINUM (*Beryllium*); Gl.; 9·1 Parsons, 9·017 Hönigschmid, occurs in *beryl, euclase, phenacite, chrysoberyl, leucophane, helvite, danalite,* and other minerals. The element was detected by Vauquelin in 1798, but the metal was first isolated by Wöhler in 1828 by fusing the chloride with potassium. Glucinum can be prepared by the electrolysis of a fused mixture of the chloride with sodium or ammonium chloride (Borschers, Chem. Zentr. 1895, ii. 13), or of the fused double fluorides, GlF_2, NaF; or GlF_2, 2NaF (Lebeau, Compt. rend. 1898, 126, 744).

Glucinum may be prepared by electrolysing the minerals containing it between metallic electrodes in the presence of fluorine or one of its compounds, either alone or with the addition of a halogen compound of an alkali or alkaline earth (Liebmann, J. Soc. Chem. Ind. 1899, 282; Eng. Pat. 3497).

Warren (Chem. News, 1895, 72, 310) describes the following process:—

Pulverised and lixiviated beryl is fused for 3 hours in a blast furnace with four times its weight of sodium carbonate, after which the solidified mass is decomposed by superheated steam, and then by hydrochloric acid, evaporated to dryness and extracted with water. The solution is now freed from iron and chromium by the acetate method, and excess of sodium carbonate added; the precipitate is treated with excess of sulphurous acid, whereby the alumina and glucina pass into solution. On boiling, the alumina is precipitated, excess of ammonium carbonate is now added to the filtered solution, which is well boiled. The precipitate of glucinum carbonate thus obtained is ignited with lampblack out of contact with air, then submitted to the action of bromine at a red heat in clay retorts, when glucinum bromide distils over and is reduced electrolytically. It is also prepared by the reduction of the oxide with aluminium (Just and Mayer, J. Soc. Chem. Ind. 1909, 528; D. R. P. 208402).

Or the finely powdered mineral is heated at 850° for half an hour with twice its weight of sodium silicofluoride. The product, which consists of silica and the double fluorides of sodium and aluminium and sodium and glucinum, is extracted three times with boiling water. The extract is filtered and to the filtrate boiling aqueous sodium hydroxide is added in slight excess. The oxide of glucinum precipitated, along with a little alumina and silica, is dissolved in sulphuric acid, and glucinum sulphate crystallises out on concentrating the solution (Copaux, Compt. rend. 1919, 168, 610).

Glucinum is a hard metal, with a bright silver-white colour, melting at 1278°±5°; sp.gr. 1·93; sp.ht. 0·4246. Glucinum has the largest heat of fusion of any metal, corresponding with its high melting-point and low atomic weight. The powdered metal takes fire when heated in air, burning with great brilliancy, and dissolves readily in dilute acids, also in caustic alkalis, with evolution of hydrogen; but it does not decompose water even at a red heat. It is generally regarded as divalent (Combes, Compt. rend. 1894, 119, 1221; Henry, *ibid.* 1895, 121, 600; Retgers, Zeitsch. physikal. Chem. 1896, 20, 481; Galecki, Zeitsch. Elektrochem. 1908, 14, 767). Tanatar (J. Russ. Phys. Chem. Soc. 1904, 36, 82; 1906, 38, 850), from various organic derivatives, regards the metal as tetravalent.

Glucinum yields useful alloys with various metals by heating the oxides with carbon in the electric furnace, or by the electrolysis of a mixture of the fused metal with the double fluoride of glucinum and sodium in a carbon crucible as anode. The 5 p.c. alloy with copper is malleable readily filed and polished, and unaffected by air; an alloy containing less glucinum is sonorous (Lebeau, Compt. rend. 1897, 125, 1172; 126, 744; Liebmann, D. R. P. 94507, 1896; Chem. Zentr. 1898, i. 484).

Glucinum alloys readily with aluminium (U.S. P. 1254987, 1918), and it is claimed that the alloys are harder, stronger, and lighter than aluminium, melt at a higher temperature, take a high polish, and make excellent castings.

Compounds. *Glucinum oxide* or *glucina* GlO is obtained from beryl by heating the coarsely powdered mineral with 6 parts of ammonium hydrogen fluoride for 10–12 hours at a temperature not exceeding a dull red heat The mass is then treated with water, and the insoluble aluminium fluoride removed by filtration. The filtrate is evaporated to dryness, and heated with strong sulphuric acid, thus removing fluorine and silica. The solution obtained on adding water is treated with nitric acid to oxidise iron, and the filtered liquid is poured into an excess of ammonium carbonate solution. Hot water is now added, after which the solution is filtered, mercuric chloride added, and the remaining iron is precipitated with ammonium sulphide. The filtered solution is boiled, whereupon basic glucinum carbonate is precipitated, which, on ignition, yields pure glucina (Gibson, Chem. Soc. Trans. 1893, 909; Lebeau, Compt. rend. 1895, 121, 641; Pollok, Chem. Soc. Trans. 1904, 603). Various other methods of preparing glucina from minerals have been described by Krüss and Moraht (Ber. 1890, 23, 727), and by Bran and Oordt (J. Soc. Chem. Ind. 1906, 1147; Eng. Pat. 15973, 1906).

It is a white amorphous powder of sp.gr. 3·016, which fuses at 2450°±50°, volatile near its melting-point, and forming, after cooling, a crystalline mass, which is harder than ruby In the electric furnace it is reduced by, and forms crystalline compounds with, boron, silicon, and carbon (Lebeau, Compt. rend. 1896, 123, 818). Heat of formation 135·9±0·9 p.c. (Mielenz and v. Wartenberg).

The oxide acts as a feeble acid towards strong bases, forming the salts $Gl(OK)_2$, whilst with feeble acids it acts as a base, yielding such salts as $(GlSO_3)_x{\cdot}GlO$ (Krüss and Moraht, *l.c.*; Seubert and Elten, Zeitsch. anorg. Chem. 4, 44). It is insoluble in water, but dissolves in strong sulphuric acid, yielding the sulphate, and also in fused potassium fluoride (Duboin, Compt. rend. 1896, 123, 698). According to Winkler (Ber. 1891, 24, 1966), when the oxide is heated with magnesium at red heat in a current of hydrogen, *glucinum hydride*, having an unpleasant smell and slowly decomposed by warm water is formed.

Glucinum hydroxide $Gl(OH)_2$ is formed by precipitating glucinum salts with ammonia, and can be separated from aluminium and iron by digestion with glacial acetic acid, when it is converted into a basic glucinum acetate, which is readily soluble in chloroform (Haber and Oordt, Zeitsch. anorg. Chem. 1904, 40, 465; D. R. P. 155466; Oordt, J. Soc. Chem. Ind. 1904, 799).

Glucinum hydroxide, when freshly precipitated, is gelatinous, readily absorbs carbon dioxide, and is soluble in dilute acids, alkalis, and alkali carbonates. On being heated with water, alkali carbonates, or ammonia, or when allowed to stand for some time at the ordinary temperature, it loses the above-described properties (Haber and Oordt, Zeitsch. anorg. Chem. 1904, 38, 377; D. R. P. 165488; *cf.* Bleyer and Kaufmann, Zeitsch. anorg. Chem. 1913, 82, 71). Unlike aluminium hydroxide, glucinum hydroxide is quite insoluble in ammonia, or in methyl- or ethylamine (Renz, Ber. 1903, 36, 2751). It combines with hydrogen peroxide to form the compound $3GlO,4H_2O_2,8H_2O$, containing hydrogen peroxide of crystallisation. A *basic peroxide* $2GlO_2,3GlO,8\frac{1}{2}H_2O$ is formed by treating basic glucinum carbonate $GlCO_3,5GlO,8H_2O$ with hydrogen peroxide which is moderately stable and exhibits all the usual properties of peroxides (Komarovski, J. Russ. Phys. Chem. Soc. 1913, 45, 608).

Glucinum chloride $GlCl_2$ is formed by passing a current of dry chlorine over a mixture of the oxide and sugar charcoal, heated to bright redness in a porcelain tube (Pollok, Chem. Soc. Trans. 1904, 604). Heat of formation 112·6±0·4 p.c. (Mielenz and v. Wartenberg: Zeitsch. anorg. Chem. 1921, 116, 267). It forms white needle-shaped crystals, melting at 400°, and boiling at about 500°. It forms a hydrated chloride $GlCl_2,4H_2O$, and also double salts with platinum, tin, and mercuric chloride, and with iodine trichloride (Weinland and Schlegelmilch, Zeitsch. anorg. Chem. 1902, 30, 134).

Glucinum iodide GlI_2 is obtained by heating the carbide in a stream of hydriodic acid, carrying iodine vapour; it melts at 510°, combines with ammonia to form $2GlI_2,3NH_3$; and yields crystalline compounds with aniline, pyridine, and other organic bases. With bromine it yields the corresponding bromide (Lebeau, Compt. rend. 1898, 126, 1272). It forms a double salt with lead iodide (Mosnier, Ann. Chim. Phys. 1897, 12, [vii.] 374).

Glucinum fluoride is obtained by the action of hydrofluoric acid on the oxide. It is soluble in water and alcohol, melts at 800°, and is converted by oxygen into the oxyfluoride $5GlF_2,2GlO$ (Lebeau, *l.c.*; and 1418).

Glucinum carbonates. Basic carbonates are formed when a glucinum salt is treated with an alkali carbonate. If carbon dioxide be passed through the aqueous solution or suspension of the basic carbonate, and the solution then evaporated in an atmosphere of carbon dioxide, the normal salt $GlCO_3,4H_2O$ separates.

The glucinum borate $5GlO,B_2O_3$, described by Krüss and Moraht, is probably a solid solution of boric acid in glucinum hydroxide. According to Bleyer and Paczuski, no definite compounds are formed by the interaction of glucinum hydroxide with aqueous solutions of boric acid.

Glucinum sulphide is a white amorphous mass, not decomposed by water, but readily by acids, even carbonic acid. It burns with a bright flame in contact with strong nitric acid and is decomposed by chlorine or bromine with formation of the respective haloid compounds. It is prepared by heating glucinum chloride in a current of hydrogen sulphide (Miebeilner and Steinmetz, Zeitsch. anorg. Chem. 1913, 82, 92).

Glucinum sulphates. The following sulphates have been obtained: $GlSO_4,6H_2O$; $GlSO_4,4H_2O$; $GlSO_4,2H_2O$; $GlSO_4,H_2O$; $GlSO_4$ (Parsons, J. Amer. Chem. Soc. 1904, 26, 1433; Len Malvano, Zeitsch. anorg. Chem. 1906, 48, 446). The anhydrous salt obtained at 250° is stable up to 530°–540°, and thus allows of the estimation of glucinum in the form of its sulphate Glucinum sulphate does not form acid salts even when dissolved in sulphuric acid. Also the *thiosulphate* $GlS_2O_3,11H_2O$ (Faktor, Chem. Zentr. 1901, ii. 878); and *sulphites* (Seubert and Elten, Zeitsch. anorg. Chem. 4, 44).

Glucinum chromate $GlCrO_4,H_2O$ has been obtained by evaporating a solution of the carbonate in concentrated chromic acid. It forms reddish-yellow crystals, which are decomposed by water, forming the basic salt $GlCrO_4,6Gl(OH)_2$, which can also be obtained by precipitating glucinum sulphate with ammonium chromate (Glassmann, Ber. 1907, 40, 2402).

Glucinum carbide GlC_2 is obtained by heating the oxide with carbon in the electric furnace (Henry, Compt. rend. 1895, 121, 600; Lebeau, *ibid.* 496). It forms microscopic yellowish-brown crystals, which scratch quartz, and are decomposed by water with formation of pure methane. Also decomposed by hot concentrated alkalis, and by halogen acids, yielding the corresponding halide.

Glucinum nitride Gl_3N_2 is obtained by heating the metal in nitrogen, or, better, in ammonia or cyanogen. Melts at 2200°, and solidifies to colourless crystals which scratch glass, stable in air, and only slowly decomposed by boiling water. Chemical properties similar to those of aluminium nitride, but is decomposed more readily by dilute acids and hot concentrated alkali hydroxides.

Glucinum borocarbide $C_4B_6Gl_6$, obtained when glucina is heated with boron in a carbon boat in the electric furnace, forms brilliant crystals with a metallic lustre; sp.gr. 2·4, readily soluble in acids, and not decomposed by water (Lebeau, Compt. rend. 1898. 126, 1347).

Glucinum phosphates (Rammelsberg, Chem. Zentr. 1891, ii. 790; Sestini, Gazz. chim. ital. 20, 313; Ouvrard, Compt. rend. 1890, 110, 1333); *arsenates* (Bleyer and Müller, Zeitsch. anorg. Chem. 1912, 75, 285); *phosphates*, *phosphite*, and *hypophosphite* (*ibid.* 1912, 79, 263); *tungstates* and *silico-tungstates* (Tanatar and Kurowski, J. Russ. Phys. Chem. Soc. 1909, 41, 813; Wyrouboff, Bull. Soc. Franc. Min. 1896, 19, 240), *molybdates* (Rosenheim and Wose, Zeitsch. anorg. Chem. 1897, 15, 283, 306, 307), and *columbates* (Larsson, *ibid.* 1896, 12, 188), *metavanadate* (Brinton, J. Amer. Chem. Soc. 1916, 38, 2361) have been obtained. Organic acids react with glucinum carbonate, forming salts of the type Gl_4OX_6, $Gl_4OX_2X'_4$, and $Gl_4OX_3X'_3$ (X, X′ being organic radicles) (Tanatar and Kurowski, J. Russ. Phys. Chem. Soc. 1907, 39, 936; Lacombe, Compt. rend. 1902, 134, 772; Glassmann, Ber. 1908, 41, 33; Parsons and Sargent, J. Amer. Chem. Soc. 1909, 31, 1203).

Glucinum basic acetate $GlO_4(CH_3CO_2)_3$ is readily soluble in chloroform and may be distilled unchanged (b.p. 330°). By this means glucinum may be separated quantitatively from iron and aluminium.

Other organic compounds of glucinum are described by Wyrouboff (*l.c.*); Kurowski (J. Russ. Phys. Chem. Soc. 1907, 39, 1630; 1908, 40, 580, 787); Curtius and Rissom (J. pr. Chem. 1898, [ii.] 58, 261); Glassmann (Ber. 1907, 40, 3059; Chem. Zeit. 1907, 31, 8).

GLUCONASTURTIIN, GLUCOTROPÆOLIN *v.* GLUCOSIDES.

GLUCOSAMINE *v.* CARBOHYDRATES.

GLUCOSE *v.* CARBOHYDRATES.

GLUCOSIDES. The glucosides are a large and important group of substances occurring almost exclusively in the vegetable kingdom, which, by the operation of hydrolysis, involving the addition of the elements of water, are resolved into sugar and another compound not belonging to the class of carbohydrates. The sugar thus formed is usually glucose or rhamnose; certain glucosides yield other carbohydrates, some of which have not yet been identified.

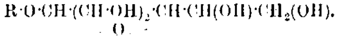
The hydrolysis may often, but not always, be rapidly effected by heating with dilute acids. It may also be brought about by the action of appropriate enzymes, such as emulsin, myrosin, &c.

Glucosides are, in many cases, far more resistant to hydrolysis by acids than is generally supposed, and almost invariably their behaviour towards acids is in marked contrast to the ease with which they are hydrolysed by the appropriate enzyme. There is some evidence that the nature of the acid is not without influence, some glucosides being more easily hydrolysed by hydrochloric than by sulphuric acid.

As a rule, a plant containing a glucoside also contains a corresponding enzyme capable of hydrolysing it. the enzyme being present also in allied species which do not contain the glucoside. On the other hand, the elder (*Sambucus nigra*, Linn.) affords an example of a plant containing a glucoside, accompanied by very little of the corresponding enzyme. Enzyme and glucoside do not exist in the same cell, but they are brought together should the cellular structure be damaged or rendered permeable.

In the greater number of cases only one variety of sugar is formed on hydrolysing a glucoside, although, in some instances, two different carbohydrates are produced, or possibly two or more glucose molecules; in such cases the simple sugar molecules are probably united as di- or tri-saccharides. Using appropriate enzymes or acids of different degrees of concentration, it is possible to remove the sugar groups one at a time, and so form new glucosides. Thus, from amygdalin, by the action of the enzyme amygdalase, which is present in some varieties of yeast, the glucoside of mandelonitrile is formed together with glucose.

The majority of the glucosides are colourless, crystalline neutral compounds, one or two are basic, and a few are acidic. They are usually soluble in water and alcohol, and but very sparingly soluble in ether. They crystallise with one or more molecules of water, which is lost on heating. They are charred when heated to a moderately high temperature, occasionally a sublimate of the non-sugar component being obtained. They are not acted upon by Fehling's solution, so far as the sugar part of the molecule is concerned. Many of them are optically active, and, as a rule, rotate rays of polarised light to the left, although derived from a dextro-rotatory carbohydrate. Pictet and Goudet (Helv. Chim. Acta, 1919, 2, 698) consider that this property may be due to the glucosides containing a glucosan rather than a glucose ring structure, since they have obtained *l* glucosan by distillation under reduced pressure of a number of glucosides. They have often a bitter taste, and a therapeutic action, being the active principle of many plant extracts used in pharmacy. The general behaviour of the glucosides and their close relationship to the synthetic methyl glucosides (*v.* CARBOHYDRATES) establishes their structure beyond doubt as :



$$\mathrm{R\cdot O\cdot \underbrace{CH\cdot(CH\cdot OH)_2\cdot CH}_{O}\cdot CH(OH)\cdot CH_2(OH).}$$

In many instances the radicle R is a polyhydroxy- compound, and it is not in all cases certain to which of the hydroxyl groups the sugar residue is attached.

It is further of interest that no natural glucoside has been found in two stereoisomeric forms corresponding to the *a*- and *β*-methyl glucosides. Judging from their behaviour towards the emulsin of almonds, many of the natural compounds are considered to be derived from *β-glucose*. This view has been confirmed in some instances by the fact that glucose is first separated as the *β*- form of low rotatory power on hydrolysing the glucoside, and afterwards undergoes isomeric change to the equilibrated mixture of *a*- and *β*-glucose. In fact, no glucosidic derivative of *a*-glucose has yet been described as occurring naturally.

In addition to a few of the natural glucosides of plants, other glucosides have been prepared in the laboratory. The isomeric *a*- and *β*-methyl glucosides are discussed under CARBOHYDRATES; glucosides of primary alcohols, *e.g.* ethyl, glyceryl, and benzyl glucosides, are obtained by the same method by the interaction of glucose and alcohol in presence of hydrogen chloride.

An alternative method first used by Colley involves the interaction of tetraacetylchloroglucose $C_6H_7OCl(OAc)_4$, and the sodium derivative of alcohols or phenols. Sodium chloride and the tetraacetate of the desired glucoside are formed, and the latter is subsequently hydrolysed to eliminate the acetyl groups. In this way the natural compounds, helicin, methylarbutin, and a number of new glucosides, including those of the terpenes and of some thiophenols, have been prepared.

Acetylbromoglucose. The employment of crystalline acetylbromoglucose in synthetic work has been extensively adopted, and Emil Fischer in particular has prepared a number of new types of glucoside by this means. The method has been modified according to the nature of the non-sugar compound employed, and the variants on the general method may be summarised as follows :—

(*a*) Treatment of silver salts of purines, thiourethanes, &c., with acetobromoglucose ;

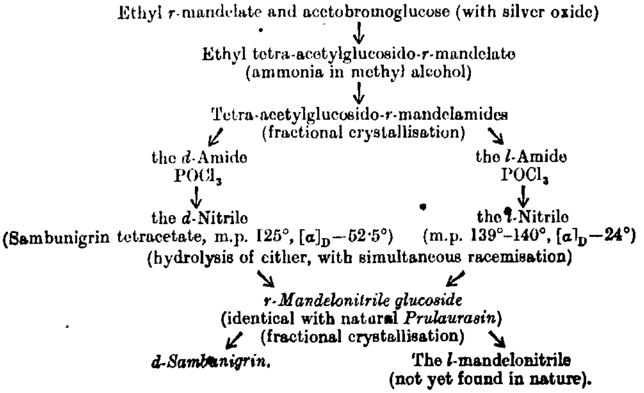
(*b*) Treatment of alcohols or phenols with the reagent and silver oxide in ether ;

(*c*) Shaking an alkaline solution of a phenol with an ethereal solution of acetobromoglucose ;

(*d*) Treatment of phenolic compounds and the reagent in presence of a small quantity of quinoline.

The main types of synthetic glucosides obtained by these reactions can be classified in a few groups :—

Mandelonitrile glucosides (E. Fischer and Bergmann, Ber. 1917, 50, 1047). An interesting sequence of reactions has led to the synthesis of several of the naturally-occurring mandelonitrile glucosides ; the work may be represented schematically as follows :—



Ethyl *r*-mandelate and acetobromoglucose (with silver oxide)
↓
Ethyl tetra-acetylglucosido-*r*-mandelate
(ammonia in methyl alcohol)
↓
Tetra-acetylglucosido-*r*-mandelamides
↙ (fractional crystallisation) ↘
the *d*-Amide
$POCl_3$
↓
the *d*-Nitrile
(Sambunigrin tetracetate, m.p. 125°, $[\alpha]_D-52{\cdot}5°$)

the *l*-Amide
$POCl_3$
↓
the *l*-Nitrile
(m.p. 139°–140°, $[\alpha]_D-24°$)

(hydrolysis of either, with simultaneous racemisation)
↘ ↙
***r*-Mandelonitrile glucoside**
(identical with natural *Prulaurasin*)
↙ **(fractional crystallisation)** ↘
***d*-Sambunigrin.**
The *l*-mandelonitrile
(not yet found in nature).

The glucoside *linamarin*, which occurs in nature, has also been synthetically prepared by E. Fischer by a similar series of reactions.

Purine glucosides (E. Fischer, Ber. 1914, 47, 210, 1058, 1377, 3193). By union of the silver derivatives of purines with acetobromoglucose. followed by removal of the acetyl groups by means of ammonia, glucosides, galactosides, and rhamnosides of adenine, guanine, hypoxanthine, theophylline, theobromine, &c., have been prepared; theophylline glucoside was further condensed with phosphoryl chloride in pyridine solution, yielding thereby *hydrated theophyllineglucosidophosphoric acid* (a synthetic nucleotide). The method of preparation has been patented by Bayer & Co. (D. R. P. 281008).

Glucosides of complex alcohols. Glucosides of geraniol, cyclohexanol, &c., have been prepared by treating the ethereal solution of the alcohol and acetobromoglucose with silver oxide (E. Fischer and Helferich, Annalen, 1911, 383, 69).

Sitosterol and cholesterol glucosides, closely resembling the phytosterolines, were synthesised by Salway (Chem. Soc. Trans. 1913, 103, 1022).

Phenol glucosides. Phloroglucinol-, resorcinol-, and 2.4.6-tribromophenol-*d*-glucosides were obtained by E. Fischer and Strauss (Ber. 1912, 45, 2467) by shaking the alkaline phenolic solution with an ethereal solution of acetobromoglucose and subsequent removal of acetyl groups. The former compound is identical with the glucoside obtained from phloridzin by Cremer and Seuffert (Ber. 1912, 45, 2565), and is capable of producing diabetes.

A mixture of α- and β glucosides was prepared by warming phenols (*e.g.* resorcinol) or menthol with acetobromoglucose in presence of quinoline (E. Fischer and von Mechel, Ber. 1916, 49, 2813; E. Fischer and Bergmann, Ber. 1917, 50, 711).

Arbutin has been prepared completely free from methyl arbutin by synthesis from acetobromoglucose and quinol in presence of alkali (Mannich, Arch. Pharm. 1912, 250, 547).

Gluco-*p*-oxybenzophenone, m.p. 178°–179°, $\alpha]_D-56°$, and gluco-*p*-acetophenone have been similarly synthesised. The latter, synthesised by Mauthner in 1912, is identical with Tanret's *picein*, isolated from pine needles (Mauthner, J. pr. Chem. 1913, [ii.] 88, 764).

Glucosides of phenolcarboxylic acids have been similarly prepared by employing the glucose reagent with an alkaline solution of the methyl ester of the acid, followed by subsequent hydrolysis; gluco-*m*-oxybenzoic acid, $C_{13}H_{16}O_8$, melts at 143°–144°, and has $[\alpha]_D-68°$ (Mauthner, J. pr. Chem. 1911, [ii.] 83, 556).

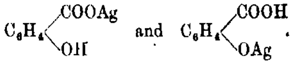
Interaction of acetobromoglucose and silver salicylate (P. Karrer, Ber. 1917, 50, 833) in boiling toluene solution yields two isomeric substances, *tetra-acetylglucose salicylate*

$$C_6H_4(OH){\cdot}COO{\cdot}C_6H_7O_5Ac_4$$

crystals, m.p. 185°, and *salicylic acid tetra-acetylglucoside* $COOH{\cdot}C_6H_4{\cdot}O{\cdot}C_6H_7O_5Ac_4$, lævorotatory, m.p. 167°.

The former gives a violet coloration with ferric chloride, and with methyl-alcoholic ammonia yields salicylamide; the latter gives no coloration, and is soluble without fission in very dilute aqueous ammonia.

The formation of these two isomerides is attributed to the coexistence of two modifications of silver salicylate:—



$$C_6H_4\begin{cases}COOAg\\OH\end{cases} \text{ and } C_6H_4\begin{cases}COOH\\OAg\end{cases}.$$

It has been shown in addition (Karrer, Nägeli and Weidmann, Helv. Chim. Acta, 1919, 2, 242; 1921, 4, 130) that the silver salts of many *d*-hydroxy- and *d*-amino- acids give a mixture of glucoside and glucose esters of the acids, whereas *m*- or *p*-hydroxy acids yield only glucose esters.

Mustard oil glucosides. Schneider and collaborators (Ber. 1914, 47, 1258, 2218, 2225) have synthesised glucosides of the general formula $R.N:C(OEt).S.C_6H_{11}O_5$ from acetylbromoglucose and silver salts of thiourethanes, the silver salt of thioglucose being obtained as a by-product.

Anhydromethylglucoside (E. Fischer and Zach, Ber. 1912, 45, 456, 2068). When triacetylmethylglucoside bromohydrin is warmed with baryta solution, anhydromethylglucoside is produced, and distils without decomposition at very low pressures. The anhydrosorbitol obtained from it by reduction is isomeric with *styracitol* (found in *Styrax obassia*) (Asahina), and suggests that anhydrides of dextrose and of glucosides may occur in nature.

A number of glucoside-like derivatives of glucosamine, synthesised from triacetylbromoglucosamine, have been described, chiefly by J. C. Irvine and co-workers.

Aminomethylglucosides. An aminomethylglucoside was produced by methylation of triacetylbromoglucosamine (Irvine, McNicoll and Hynd, Chem. Soc. Trans. 1911, 99, 250; 1912, 101, 1128).

A second, different, aminomethylglucoside was formed by the action of ammonia upon methylglucoside (E. Fischer and Zach, Ber. 1911, 44, 132).

a-Aminohelicin and *a-aminosalicin.* These were obtained synthetically from triacetylbromoglucosamine hydrobromide and salicyl aldehyde and saligenin respectively (Irvine and Hynd, Chem. Soc. Trans. 1913, 103, 41).

Morphine glucosamine. In the preparation of aminohelicin and aminosalicin morphine was employed as the alkaline or basic condensing agent, and as by-product there appeared morphineglucosamine (Irvine and Hynd, Chem. Soc. Trans. 1913, 103, 41).

Enzyme syntheses. The synthesis of glucosides from their components by means of enzyme action has been developed by several workers, especially Bourquelot and his collaborators, whose results are described in the following papers:—

Ann. Chim. Phys. 1913, [viii.] 28, 145; Compt. rend. 1912, 155, 1552; 1913, 157, 72, 732; 156, 957; 1915, 160, 742; 161, 184.

It has been found that the same enzyme which hydrolyses a glucoside in presence of excess of water will synthesise it in presence of excess of the hydroxy-component of the glucoside; moreover, if conditions are employed in which the reagents are present in equimolecular or other definite quantities a state of equilibrium is reached which can be approached from either set of components—glucoside and water, or sugar and non-sugar component of the glucoside.

An interesting suggested application of this method as a qualitative polarimetric test for glucosides in plants has been made as follows:—the suspected material is hydrolysed by an enzyme, the change in rotation is observed, the solution heated to 100°C., and cooled, more enzyme is added, and if displacement of the rotatory power towards the original value occurs, it may be taken as an indication of the presence of a glucoside in the original material.

It may be mentioned here that Bertrand and Compton (Compt. rend. 1912, 154, 1646) assert that hydrolysis by emulsin of glucosides is not reversible.

A point arising in the course of Bourquelot's work was the discovery that, contrary to general assumption, the activity of emulsin is not invariably and completely inhibited by alcohol. Thus, *gentiopicrin* and *salicin* may be hydrolysed, at all events partially, by emulsin in comparatively concentrated alcoholic solution (Bourquelot and Bridel, J. Pharm. chim. 1911, [vii.] 4, 385; Compt. rend. 1912, 154, 944).

As examples of the general method of glucoside synthesis by enzyme action may be mentioned the preparation of methyl-, geranyl-, and cinnamyl-β-glucosides and of benzyl-β-galactoside from the corresponding alcohols and sugars in presence of emulsin. On the other hand, similar α-glucosides have been produced by the action of the enzyme (α-glucosidase) contained in the aqueous extract of bottom yeast.

The synthesis of glucosides of glycol and glycerol, difficult by other means, was effected by the enzyme method, emulsin being used. α-Glycol monoglucoside was obtained crystalline, $[\alpha]_D+135°$, and two different glyceryl monoglucosides were prepared from an aqueous solution of glycerol and glucose in presence of emulsin in the course of nine months' reaction, in the form of a hard amorphous mass, $[\alpha]_D+27°$.

Hämäläinien (Biochem. Zeitsch. 1913, 49, 398; 50, 209; 52, 409; 53, 423) has synthesised a number of glucosides of terpene alcohols by the enzyme method (emulsin), including those of: *l*-borneol, *r*-isoborneol, camphene, *d*-citronellol, cyclohexanol, dihydrocarveol, *l*-fenchyl alcohol, sabinol, santenol, *cis*-terpin, and terpineol.

The function of glucosides has been a subject of considerable discussion. They have been regarded as reserve materials; as antiseptics, and, therefore, bactericidal in character; and as protectives, on the assumption that the bitter taste and poisonous properties of many would act as a warning to animals. A more recent view is that the non-sugar constituents function as hormones; that is, they are able to penetrate the plant cells and stimulate the protoplasm to greater activity; much evidence has been adduced in favour of this view (*see* E. F. Armstrong, The Simple Carbohydrates and Glucosides, London, Longmans, 1919).

Preparation.—Glucosides are obtained from plants by extraction with water or alcohol, the abstract being subsequently purified in a variety of ways to eliminate other soluble substances. The extraction of the plant material is often conveniently performed in a Soxhlet apparatus; and ethyl acetate will sometimes be found to be a convenient solvent. It is essential in most cases to destroy the accompanying enzyme before extracting with water, so that hydrolysis may not take place.

For convenience of reference only the most important glucosides are here described in alphabetical order. They are, perhaps, better classified in groups according to the nature of the non-sugar constituent, and brief reference may therefore be made to these groupings. Special works dealing with the glucosides are: *Van Rijn*, Die Glucoside, Berlin, 1900; *Roscoe-Schorlemmer's Chemie*, Band 8, Pflanzen Glucoside, Braunschweig, 1901; *Armstrong*, The Simple Carbohydrates and Glucosides, London, 1919, in all of which numerous references to the original literature will be found.

Phenols occur very frequently as constituents of glucosides, especially those containing two and more hydroxyl groups. The sugar residue is attached to a phenolic hydroxyl rather than to an aliphatic alcohol group in a side chain, *e.g.* salicin, coniferin.

Aldehydes. A number of glucosides of benzaldehyde exist, but in most of these hydrogen cyanide is attached to the aldehyde group. The relationship of amygdalin, and the three amygdonitrile glucosides, *prulaurasin*, *sambunigrin*, and *prunasin*, is of considerable interest. *Salinigrin*, the glucoside of *m*-hydroxybenzaldehyde, is isomeric with *helicin*, the glucoside of *o*-hydroxybenzaldehyde, obtained by oxidising salicin, but not yet found in plants. *Dhurrin* is a derivative of *p*-hydroxybenzaldehyde.

Acids. Glucosides of the higher fatty acids are characteristic of the *Convolvulaceæ*, and are used as purgatives.

Coumarins. The glucosides of the coumarin group are interesting. That of coumarin itself has not yet been isolated, though there can be little doubt that coumarin, which is so widely distributed in plants, is present in this form. Skimmin is a monohydroxycoumarin; æsculin and daphnin are isomeric dihydroxycoumarins; fraxin, a trihydroxycoumarin. Scopolin is the methyl ether of æsculin.

Hydroxyanthraquinone glucosides are madder, frangulin, and others, like aloes, which form emodin on hydrolysis.

Hydroxyflavone glucosides all give yellow dyestuffs. Those described are apiin, fustin, gossypitrin, incarnitrin, quercimeritrin, quercitrin, *iso*quercitrin, robinin, rutin, serotin, vixetin, xanthorhamnin. They are mostly rhamnosides.

The following glucosides contain rhamnose: *Baptisin*, *convallamarin*, *datiscin*, *frangulin*, *fustin*, *glycyphyllin*, *hesperidin*, *kampheritrin*, *ouabain*, *naringin*, *quercitrin*, *robinin*, *rutin*, *solanin*, *strophantin*, *trifolin*, *α-turpethein*, *xanthorhamnin*.

Those containing pentoses other than rhamnose are: *Aloin*, *antiarin*, *convolvulin*, *gentiin*, *helleborein*, *jesterin*, *quinovin*, *saponin*, *β-turpethein*, *vicianin*.

The following contain galactose: *Convallamarin*, *digitonin*, *robinin*, *sapotoxin*, *solanin*. Lævulose has so far only been obtained from *alliin*, the glucoside of garlic (Rindquist, Apoth. Zeit. 1910, 25, 105).

The glucosides hydrolysed by emulsin are:

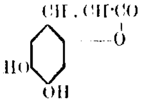
Æsculin, amygdalin, amygdonitrile glucoside, androsin, arbutin, aucubin, bankankosin, calmatambin, coniferin, daphnin, dhurrin, gentiopicrin, incarnatrin, indican, meliatin, oleuropein, picein, prulaurasin, salicin, sambunigrin, syringin, taxicatin, verbenalin.

Adonin $C_{24}H_{10}O_9$, from *Adonis amurensis* (Reg and Rada) (*v.* Tahara, Ber. 24, 2579).

Æsculin $C_{15}H_{16}O_9,2Aq$, m.p. 205°, is found in the bark of the horse chestnut (*Æsculus hippocastanum*, Linn.), and in the roots of the wild jasmin (*Gelsemium sempervirens*, Ait.). It is very sparingly soluble in cold water, and crystallises in lustrous colourless prisms. Characteristic is the blue fluorescence of the aqueous solution, even when very greatly diluted; it is evident in a solution of 1 part of æsculin in 15 million parts of water. Alkali increases the fluorescence, acids destroy it. The aqueous solution is faintly acid. It gives a yellow solution with nitric acid, which, on the addition of ammonia, acquires a deep blood-red colour (comp. Schunck and Marchlewski, Annalen, 1894, 278, 353; Gattermann and Köbner, Ber. 1899, 32, 288). By the action of warm dilute mineral acids or of emulsin at 30°, æsculin is hydrolysed to glucose+æsculetin (a dihydroyxcoumarin)

$$C_{15}H_{16}O_9+H_2O=C_6H_{12}O_6+C_9H_6O_4.$$

Æsculetin has the formula:



Æsculin is isomeric with daphnin.

Aloin, Barbaloin. The glucosides from the various species of aloe are but indefinitely characterised. They are decomposed into aloe emodin, which is a trihydroxymethyl anthraquinone identical with that derived from frangulin, and a sugar which is sometimes dextrose, sometimes a pentose. Léger (Bull. Soc. chim. 1910, 7, 479; and Compt. rend. 1910, 150, 1695) ascribes to barbaloin the formula $C_{20}H_{18}O_9$, and obtained from it on hydrolysis, emodin and *d*-arabinose. Since the arabinose, which is a constituent of gums, &c., is *l*-arabinose, the occurrence of the *d*-isomeride is remarkable, as showing that sugars of both *d*- and *l*- series occur naturally.

Amygdalin $C_{20}H_{27}O_{11}N,3Aq$, m.p. 200°, $[\alpha]_D^{28°}$ −38·3°, is the oldest known glucoside; it was first found by Robiquet and Boutron in 1830 in bitter almonds. The composition and mode of decomposition by emulsin into glucose, oil of bitter almonds, and hydrogen cyanide, was first indicated by Wöhler and Liebig. Besides the bitter almond, it is contained in the kernels of peaches, cherries, plums, apples, and in the fruits of most of the *Rosaceæ*. It crystallises from water in transparent rhombic prisms, from alcohol in glistening platelets. It is soluble in water, sparingly soluble in cold alcohol.

It is very readily hydrolysed by the emulsin of almonds to glucose (2 mols.), hydrogen cyanide, and benzaldehyde

$$C_{20}H_{27}O_{11}N+2H_2O=C_7H_6O+HCN+2C_6H_{12}O_6$$

Yeast contains an enzyme amygdalase, which hydrolyses it to glucose and amygdonitrile glucoside (*prunasin*)

$$C_{20}H_{27}O_{11}N+H_2O=C_6H_{12}O_6+C_{14}H_{17}O_6N,$$

which has since been found to occur naturally, and is, in its turn, hydrolysed by emulsin. Almond emulsin has been shown to be a mixture of three enzymes, which act consecutively.

Amygdalase first splits off one molecule of glucose, a *β-glucase* hydrolyses the amygdonitrile glucoside to *β*-glucose and *d*-mandelonitrile, and *cyanase* hydrolyses this last to benzaldehyde and hydrogen cyanide. It has not been possible to obtain the two glucose molecules from amygdalin united in the form of a disaccharide by means of plant enzymes, but using the digestive juices of the snail *Helix pomatia*, Giaja (Compt. rend. 1910, 150, 593) has demonstrated that a non-reducing disaccharide of the trehalose type is first formed, though subsequently hydrolysed to glucose. The disaccharide of amygdalin is definitely not maltose nor cellobiose. Dilute acids act as almond emulsin does; strong hydrochloric acid hydrolyses amygdalin to *l*-mandelic acid, glucose, and ammonia. Concentrated sulphuric acid gives glucose and *d*-mandelonitrile.

On treatment with baryta, the *d*-mandelonitrile group in amygdalin is racemised and *iso*amygdalin is obtained. This is hydrolysed by amygdalase to prulaurasin. (For bibliography, *see* E. F. Armstrong, The Simple Carbohydrates and Glucosides; also Walker and Krieble, Chem. Soc. Trans. 1909, 95, 1437.)

Amygdonitrile glucoside (*Prunasin*)

$$C_{14}H_{17}O_6N,$$

m.p. 147°, $[\alpha]_D$ −26°, occurs in the young branches of *Prunus* (*Cerasus*) *Padus* (Linn.) (Hérissey, Arch. Pharm. 1907, 245, 641), and in the bark of the wild cherry, *Prunus serotina* (Ehrh.) (Power and Moore, Chem. Soc. Trans. 1909, 95, 243). It is obtained from amygdalin by the action of an extract of dried yeast (Fischer, Ber. 1895, 28, 1508). This enzyme amygdalase is only present in some specimens of brewers' yeast (top fermentation). Amygdonitrile glucoside is the *β*-glucose ether of *d*-mandelonitrile, *i.e.* the nitrile of *l*-mandelic acid (*cf.* prulaurasin and sambunigrin).

Androsin $C_{15}H_{20}O_8,2Aq$, m.p. 218°–220°, found in the rhizome of *Apocynum androsæmifolium* (Linn.) (Moore, Chem. Soc. Trans. 1909, 95, 734), forms long colourless needles, sparingly soluble in cold water or alcohol, readily in hot water. On hydrolysis by emulsin or sulphuric acid, it yields glucose and acetovanillone

$$CH_3{\cdot}CO{\cdot}C_6H_3(OMe)(OH).$$

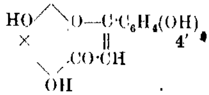
Antiarin. The latex of *Antiaris toxicaria* (Lesch.), an arrow poison, contains two glucosides. *α*-Antiarin $C_{27}H_{42}O_{10},4Aq$ crystallises in leaflets or plates; m.p. 220°–225°; it is hydrolysed to antiarose, *i.e.* a methyl pentose, and antiarigenin $C_{21}H_{30}O_5$. *β*-Antiarin

$$C_{27}H_{38}O_{10},3Aq$$

or $C_{28}H_{38}O_{10},3Aq$, crystallises in slender needles; m.p. 206°–207°. Emulsin has no action on either glucoside; both are toxic, their action resembling strophantin (Kiliani, Ber. 1910, 43, 3574).

Apiin $C_{26}H_{28}O_{14}$ (?), m.p. 228°, found in the leaves and seeds of parsley [*Carum* (*Apium*) *Petroselinum* (Bentl. and Hook.)], in celery [*A.*

graveolens (Linn.)], and other umbelliferous plants; crystallises in small colourless needles; sparingly soluble in cold, easily soluble in hot water and alcohol. The solutions readily gelatinise; they are strongly dextro-rotatory. It is hydrolysed by mineral acids with difficulty to glucose, apiose, a C_5 sugar with a branched chain of carbons (*v.* CARBOHYDRATES), and apigenin $C_{15}H_{10}O_5$, a hydroxyflavone derivative of the constitution



The sugar residue is probably united to the hydroxyl- group marked × (*see* Perkin, Chem. Soc. Trans. 1897, 71, 817).

Aralin, m.p. 260°, occurs in *Aralia japonica*. It is insoluble in water, contains no nitrogen, and does not reduce Fehling's solution. On hydrolysis it yields glucose and an acidic compound *aralidin*, which forms white crystals, m.p. 246°–248° (Danzel, J. Pharm. Chim. 1912, [vii.] 5, 530).

Arbutin $C_{12}H_{16}O_7$,1Aq, m.p. 142°, and again at 194°, $[\alpha]_D$ −63·5°, occurs in the leaves of the bear-berry [*Arctostaphylos Uva-ursi* (Spreng)], in a number of *Ericaceæ*, and in the roots, trunks, and leaves of most pear species (Bourquelot, Compt. rend. 1911, 153, 468). Excepting in the pear, it is found associated with methyl arbutin, from which it cannot be separated by crystallisation. Hérissey effects this by the addition of potassium hydroxide to crude arbutin dissolved in alcohol. The syrupy precipitate is heated with acetic acid in alcohol, calcium carbonate added when it is in solution, the alcohol distilled off, and the residue extracted with water (Bull. Soc. chim. 1910, 7, 1054). Arbutin crystallises in long silky needles, gives a blue coloration with ferric choride, and a sapphire-blue colour with Jungmann's reagent. It is hydrolysed by emulsin or by mineral acids to glucose and quinol; owing to the presence in emulsin of a small amount of oxydase, the quinol formed in this way becomes slightly oxidised, and the solution assumes a yellowish- or reddish-brown colour (*see* Bourquelot and Hérissey, Compt. rend. 1908, 146, 764; Bourquelot and Fichtenholz, J. Pharm. Chim. 1910, [vii.] 1, 62, 104; Hérissey, Compt. rend. 1910, 151, 444).

Arbutin is readily detected by moistening the powdered material with dilute hydrochloric acid, heating cautiously on an object-glass, and collecting the sublimate of quinol which forms upon a second object-glass (Tunmann, Ber. Deut. pharm. Ges. 1911, 21, 312).

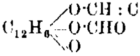
Hérissey's method for separating the arbutin of bearberries from methyl arbutin does not give pure arbutin. A better, but still imperfect, process is to separate the arbutin in the form of its additive compound with hexamethylenetetramine. Pure arbutin is produced synthetically from acetobromoglucose and quinol in presence of alkali; the compound (+1Aq) melts at 163°–164°, and again at 200°, $[\alpha]_D$ −60°.

Pure methyl arbutin melts at 158°–160°, and again at 175° (Mannich, Arch. Pharm. 1912, 250, 547).

Methyl arbutin $C_{13}H_{18}O_7$,1Aq, m.p. 175°, $[\alpha]_D$ −64°, crystallises in needles; it gives no coloration with either ferric chloride or Jungmann's reagent. It is hydrolysed by emulsin more quickly than arbutin, yielding glucose and quinolmethyl ether (Hlasiwetz and Habermann, Annalen, 1875, 177, 334). It does not darken in colour on hydrolysis in presence of an oxydase. Methyl arbutin was synthesised by Michael by the interaction of acetochloroglucose with potassium quinol methyl ether (Amer. Chem. J. 1885, 6, 336).

Aucubin $C_{13}H_{19}O_8$,1Aq, m.p. 181° $[\alpha]_D$ −174°, is found in the seed, leaves, stem, and roots of the Japanese variegated laurel, *Aucuba japonica* (Thunb.) and allied species. It also occurs in *Garrya* and *Plantago* species. It is hydrolysed by mineral acids and by emulsin to glucose and aucubigenin ($C_7H_9O_3$). The latter has not been isolated; it is condensed to an intense black-coloured product immediately it is formed. It is this compound which causes *aucuba* leaves to become black when put in an atmosphere of chloroform for a few minutes. (Literature summarised by Bourquelot and Hérissey, Ann. Chim. 1905, [viii.] 4, 289.)

Baptisin $C_{26}H_{32}O_{14}$,9Aq, m.p. 240°, $[\alpha]_D$ −61°, found in the roots of *Baptisia tinctoria* (R.Br.), crystallises in reniform aggregates of slender needles, sparingly soluble in water; it is hydrolysed to rhamnose (2 mols.) and baptigenin $C_{14}H_{12}O_6$, a phenol containing three hydroxyl groups (Gorter, Arch. Pharm. 1897, 235, 303). *ψ-Baptisin* $C_{27}H_{30}O_{14}$, 4Aq, m.p. 247°, which occurs in the same root is hydrolysed to glucose, rhamnose, and *ψ*-baptigenin $C_{15}H_{10}O_5$ or


$$C_{12}H_6\begin{cases}O\cdot CH:CH\cdot OH\\ O\cdot CHO\\ O\end{cases}$$

(Gorter, Arch. Pharm. 1907, 245, 561).

Calmatambin $C_{19}H_{28}O_{13}$,2Aq, m.p. 144°, $[\alpha]_D$ −130°, found in the bark of *Canthium glabriflorum* (Hiern.) from Sierra Leone, crystallises in colourless prismatic needles. It is hydrolysed by mineral acids and by emulsin to glucose and *Calmatambetin* $CH_3O\cdot C_{12}H_{10}O_2(OH)_3$. It is physiologically inactive (Pyman, Chem. Soc. Trans. 1907, 91, 1228).

Cedrin $C_{21}H_{26}O_8$, crystals, m.p. 265°, is found in *Sinaba cedron*, and gives by hydrolysis a sugar which has not yet been identified (Viehoever, Geiger, and Johns, J. Biol. Chem. 1916, 24).

Clavicepsin $C_{18}H_{34}O_{16}$,2Aq, m.p. 91°, and (anhydrous) at 198°, is found in *Secale cornutum*; it is not hydrolysed by emulsin, but with acids gives 2 molecules of glucose and 1 molecule of mannitol (Marino-Zuco and Pasquero, Gazz. chim. ital. 1911, 41, [ii.] 368).

Coniferin $C_{16}H_{22}O_8$,2Aq, m.p. 185°, $[\alpha]_D$ −67°, was discovered in the cambial sap of *Larix decidua* (Mill.), and occurs in the saps of the conifers in general; it is found also in beetroot and asparagus.

It crystallises in colourless rosettes of pointed needles, sparingly soluble in cold water. The aqueous solution has a slightly bitter taste. When moistened with phenol and concentrated hydrochloric acid, an intense blue colour is formed; it is soluble in concentrated sulphuric acid with a red coloration. It is decomposed by heating with mineral acids, but emulsin hydrolyses it to glucose and coniferyl alcohol $C_6H_3(OH)(OMe)C_3H_4{\cdot}OH$.

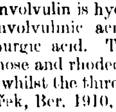
On oxidation with permanganate, glucovanillinic acid $C_6H_3(OMe)(CO_2H)OC_6H_{11}O_5$ is obtained, m.p. 211°. Chromic acid oxidises coniferin to glucovanillin, m.p. 192°, which is hydrolysed by emulsin or by acids to glucose and vanillin (*see* Tiemann and Haarmann, Ber. 1874, 7, 608; 1875, 8, 509, 1127; 1876, 9, 408, 1278).

Convallamarin and **Convallarin** are two glucosides occurring in *Convallaria majalis*; the former is soluble in water and alcohol, and has a physiological action similar to that of digitalin, whilst the latter is insoluble in water and acts only as a purgative (Reichard, Pharm. Zeit. 1911, 52, 183).

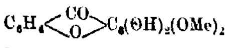
Convolvulin $C_{54}H_{96}O_{27}$, m.p. 150°, is found in jalap root, *Ipomœa purga* (Hayne). It is a colourless amorphous powder, very sparingly soluble in water, but readily soluble in alcohol and acetic acid, and dissolves in concentrated sulphuric acid with a red coloration. It is hydrolysed by acids to dextrose, rhodeose, and convolvulinolic acid $C_{15}H_{30}O_3$. This acid, on oxidation, takes up 2 molecules of oxygen, forming methylethyl acetic acid and ipomic acid $C_{10}H_{18}O_4$, an isomeride of sebacic acid (*cf.* Votoček, Ber. 1910, 43, 476).

Convolvulin is hydrolysed by aqueous baryta to convolvulinic acid, α-methyl butyric acid, and purgic acid. The first-named acid yields rhamnose and rhodeose by the action of mineral acids, whilst the third similarly gives isorhodeose (Votoček, Ber. 1910, 43, 476).

Cymarin $C_{30}H_{44}O_9$, m.p. 130°–138°, $[\alpha]_D + 23°$, occurs in *Apocynum cannabinum*; by hydrolysis are produced *Cymarose* $C_7H_{14}O_4$, m.p. 88°, which is probably a methyl ether of digitoxose, and *cymarigenin*, $C_{23}H_{30}O_5$, melting at 171°, a lactone, said to be identical with the strophanthidin of Feist (whose formula $C_{27}H_{38}O_6$ is said to be wrong). Cymarin is similar in physiological action to strophanthin and digitoxin; the only difference between cymarin and strophanthin is the different sugar constituent (Windaus and Hermanns, Ber. 1915, 48, 979, 991).

Daphnin $C_{15}H_{16}O_9,2Aq$, m.p. 200°, is a constituent of the bark of *Daphne mezereum* (Linn.) and *D. alpina* (Linn.). It forms long colourless needles or prisms, sparingly soluble in water, easily soluble in alcohol. It is faintly acid, and has a bitter astringent taste. It is soluble in alkalis and their carbonates with a golden-yellow colour, the solutions decompose on boiling. On hydrolysis by acids or by emulsin, glucose and daphnetin  are formed (comp. Stünkel, Ber. 1879, 12, 109).

Datiscin $C_{21}H_{24}O_{11},2Aq$, m.p. 190°, present in the leaf and roots of *Datisca cannabina* (Linn.), forms colourless lustrous needles. On hydrolysis by acids rhamnose and datiscetin



$$C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{O}{>}C_6(OH)_2(OMe)_2$$

are formed (Schunck and Marchlewski, Annalen, 1893, 277, 261; 1894, 278, 351).

Dhurrin $C_{14}H_{17}O_7N$ was obtained from the great millet, *Sorghum vulgare* (Pers.), by Dunstan and Henry (Phil. Trans. 1902, A, 199, 399). It is hydrolysed by emulsin and by dilute hydrochloric acid to glucose, hydrogen cyanide, and *p*-hydroxybenzaldehyde. It is the glucoside of *p*-hydroxymandelonitrile.

Dibenzoylglucoxylose, $C_{25}H_{28}O_{12},1Aq$, described by Power and Salway (Trans. Chem. Soc. 1914, 105, 767, 1062), is an entirely new type of naturally-occurring glucoside. It occurs in *Daviesia latifolia*. M.p. 147°–148°, $[\alpha]_D - 107°$, in methyl alcohol. It has a very bitter taste, is sparingly soluble in cold water, ether, or chloroform, but readily in hot water or in alcohol. It does not reduce Fehling's solution. The penta-acetate has m.p. 203°.

Digitalis glucosides. The leaves and seed of the foxglove, *Digitalis purpurea* (Linn.), contain glucosides, which increase the activity of all forms of muscle tissue, more especially that of the heart and arterioles. The leaves contain digitalin, digitoxin, and, perhaps, digitalein, the existence of this as an entity being uncertain. The seeds contain digitalin and digitonin, a glucoside of the saponin class, which is possibly also present in the leaves (*v.* DIGITALIS).

Digitalin $C_{35}H_{56}O_{14}$ or $C_{36}H_{58}O_{14}$, m.p. 217°, is obtained from commercial German digitalin by extraction with ether-alcohol. It occurs in characteristic colourless granular masses, and crystallises in needles from 85 p.c. methyl alcohol. It is very sparingly soluble in cold water, readily in alcohol. Concentrated sulphuric acid dissolves it with a golden-yellow coloration, which changes to a magnificent rose-red or violet-red on the addition of potassium hypobromite. Sulphuric acid containing a little ferric oxide gives, with digitalin, at first an intense golden-yellow, and then a red colour changing to a permanent reddish-violet.

It is hydrolysed on heating with dilute alcoholic hydrogen chloride to glucose, a sugar $C_7H_{14}O_5$ named digitalose, and digitaligenin $C_{22}H_{30}O_3$ or $C_{23}H_{32}O_3$, which last crystallises in granular aggregates of needles; m.p. 210°. Digitalin possesses the characteristic action on the heart without being cumulative.

Digitonin $C_{54}H_{92}O_{28}$ or $C_{55}H_{94}O_{28}$, m.p. 225°, $[\alpha]_D - 50°$, forms one-half of the mixed glucosides from digitalis seed, and the principal proportion of commercial German digitalin. To obtain it the commercial product is dissolved in 85 p.c. alcohol at 50°–60°, and allowed to crystallise slowly; digitonin then separates. When pure it crystallises in crusts of slender needles, very sparingly soluble in water, readily soluble in alcohol. The hot aqueous solution is opalescent, and the glucoside does not separate on cooling. The aqueous solution froths like that of saponin. It gives a red coloration with concentrated sulphuric acid, and, on heating with concentrated hydrochloric acid, becomes yellow, then red, and finally somewhat blue. It is hydrolysed on heating with alcoholic hydrogen chloride to glucose (2 mols.), galactose (2 mols.), and digitogenin $C_{30}H_{48}O_6$ or $C_{31}H_{50}O_6$, crystallising in slender needles, which soften at 250°. Digitonin is poisonous, but does not possess the action on the heart peculiar to digitalis. It forms crystalline compounds with amyl alcohol and other alcohols, and with phenol, and combines with I mol. cholesterol in alcoholic solution to give a crystalline precipitate, which is no longer poisonous. This is a valuable test for digitonin.

Digitoxin $C_{34}H_{54}O_{11}$, the most active principle of digitalis leaves, is cumulative in its action; it is the chief constituent of 'Nativelle's crystallised digitalin,' or 'French digitalin.' It is obtained by extracting the leaves with water, and then with alcohol, precipitating the alcoholic solution with lead acetate, evaporating and extracting the residue with chloroform. It crystallises from chloroform in thin anhydrous prisms, which are not melted at 240°, and from dilute alcohol in hydrated crystals; m.p. 145°. It is insoluble in hot or cold water, soluble in alcohol, chloroform, or ether. When it is dissolved in glacial acetic acid, a drop of ferric chloride added, and then concentrated sulphuric acid is cautiously poured down so as to form a layer under the acetic acid, a dirty brownish-green band appears, which alters to a broad intense bluish-green band at the dividing zone. It is hydrolysed by alcoholic hydrogen chloride at the ordinary temperature to digitoxigenin $C_{22}H_{32}O_4$, colourless crystals, m.p. 230°, and 2 molecules digitoxose $C_6H_{12}O_4$, a sugar having the constitution:

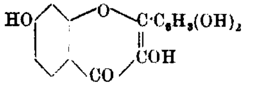
$$CH_3{\cdot}CH(OH){\cdot}CH(OH){\cdot}CH(OH){\cdot}CH_2{\cdot}CHO.$$

It crystallises in prisms, m.p. 102°, and is dextro-rotatory (*cf.* Kiliani, Arch. Pharm. 1913, 251, 562–580; Ber. 1915, 48, 334).

Frangulin $C_{21}H_{20}O_9$, m.p. 228°, found in the bark, root bark, seeds, and fruit of the berry-bearing alder, *Rhamnus frangula* (Linn.), and also in *R. carthartica* (Linn.), is a yellow silky glistening microcrystalline powder, nearly insoluble in water, readily soluble in alcohol and benzene. It dissolves in alkalis with an intense cherry-red colour. It is hydrolysed by acids to rhamnose and emodin (trihydroxymethylanthraquinone) (comp. Schwabe, Arch. Pharm. 1888, 226, 569; Thorpe and Miller, Chem. Soc. Trans. 1892, 61, 1).

Fraxin $C_{16}H_{18}O_{10}$, m.p. 320°, obtained from the bark of the ash *Fraxinus excelsior* (Linn.), and from several *Æsculus* and *Pavia* species, crystallises in colourless needles, sparingly soluble in cold water, but easily in hot water and alcohol. The solutions, like those of æsculin, fluoresce blue. It is hydrolysed by dilute sulphuric acid to glucose and fraxetin $C_{10}H_8O_5$, the monomethyl ether of a trihydroxycoumarin. It contains a methoxyl group more than daphnin or æsculin (*see* Rochleder, Wien. Akad. Ber. 1863, 48, 230).

Fustin $C_{36}H_{28}O_{14}$, m.p. 218°, the glucoside of fustic (*Rhus cotinus* [Linn.]), forms small needles of silvery lustre. Dilute sulphuric acid hydrolyses it to rhamnose and 2 molecules of fisetin $C_{15}H_{10}O_6$, which is a 3 : 3′ : 4′-trihydroxyflavonol of the following constitution:



(*see* Perkin, Chem. Soc. Trans. 1897, 71, 1194).

Gaultherin $C_{14}H_{18}O_8$,1Aq, decomposes at 100°, found in *Gaultheria procumbens* (Linn.), *Betula lenta* (Linn.), *Monotropa Hypopitys* (Linn.), *Spiræa ulmaria* (Linn.), *S. filipendula* (Linn.), and other plants, forms prismatic crystals, easily soluble in water and alcohol. It is hydrolysed by mineral acids and by a specific enzyme, gaultherase, which accompanies it in plants. Emulsin is without action. The products of hydrolysis are glucose and methyl salicylate $C_6H_4(OH)CO_2CH_3$ (*see* Bourquelot, Compt. rend. 1896, 122, 1002).

Gentiacaulin, $[\alpha]_D -64°$, occurs in *Gentiana acaulis*, and gives glucose and xylose on hydrolysis; the non-sugar constituent is not stated (Bridel, J. Pharm. Chim. 1914, [vii.] 10, 329).

Gentiin $C_{25}H_{28}O_{14}$, m.p. 274°, occurring in the root of the gentian (*Gentiana lutea* [Linn.]), crystallises in yellow needles. It is hydrolysed to dextrose, xylose, and gentienin $C_{14}H_{10}O_5$, which is isomeric with gentisin..

Gentiopicrin $C_{16}H_{20}O_9$,½Aq, m.p. 120°–125°, or anhydrous at 191°, $[\alpha]_D -198°$, which is likewise a constituent of gentian root (Tanret, Chem. Soc. Abstr. 1905, i. 655, 714), occurs also in a number of species of *Gentiana*, and in *Blackstonia* (*Chlora*) *perfoliata* (Huds.). It is hydrolysed by emulsin to dextrose and gentiogenin (comp. Bourquelot and Bridel, J. Pharm. Chim. 1910, [vii.] 1, 156).

Gitalin $C_{28}H_{48}O_{10}$, m.p. 150°–155°, was obtained from *Digitalis* leaves by extraction with cold water and then with chloroform. It is said to be the chief constituent of commercial digitalin, is a white, neutral amorphous powder, soluble in 600 parts of water. It crystallises from a mixture of 2 parts alcohol and 1 part water with $4H_2O$, the hydrate melting at 75°.

When an alcoholic solution of gitalin is evaporated in a vacuum *anhydrogitalin*, $C_{28}H_{46}O_9$, m.p. 255°, is produced; this is insoluble in water and chloroform, but dissolves in 800 parts of boiling alcohol.

Hydrolysis in alcoholic HCl solution of *anhydrogitalin* yields digitoxose and *anhydrogitaligenin* $C_{22}H_{34}O_5$, melting at 216°–219° (Kraft, Schweiz. Wochensch. Chem. Pharm. 1911, Nos. 12, 13, and 17; Arch. Pharm. 1912, 250, 118).

Kiliani (Arch. Pharm. 1913, 251, 562) did not succeed in transforming Kraft's *gitalin* into *anhydrogitalin* by absolute alcohol; the same writer (Arch. Pharm. 1914, 252, 13) separated *gitalin* into a number of fractions differing in physiological action, solubility and behaviour on hydrolysis by treatment with water and a mixture of methyl alcohol, chloroform, and ether.

Kiliani is supported by the similar work of Rosenthaler (Chem. Zeit. 1914, ii. 328).

Gitin, m.p. 265°, was also extracted from *Digitalis* leaves by Kraft (Arch. Pharm. 1912, 250, 118). It crystallises in long needles, insoluble in water; it is isomeric with *digitonin*, but contains galactose in place of glucose. It is physiologically inactive.

Gitonin $C_{49}H_{80}O_{23}$, decomposes at 272°, $[\alpha]_D -51°$, is an amorphous glucoside found in Merck's digitonin. It forms an additive compound with cholesterol, and on hydrolysis is resolved into 3 molecules galactose, 1 molecule pentose, and *gitogenin* $C_{26}H_{42}O_4$, a crystalline compound melting at 271°–272° (Windaus and Schreckenburger, Ber. 1913, 46, 2628).

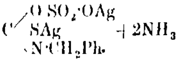
Glucocheirolin $C_{11}H_{20}O_{11}NS_3K,Aq$, colourless needles, m.p. 158°–160°, $[\alpha]_D -21°$, occurs in wallflower seeds. Its constitution is probably:

$$CH_3{\cdot}SO_2{\cdot}CH_2{\cdot}CH_2{\cdot}N(O{\cdot}SO_3K){\cdot}S{\cdot}C_6H_{11}O_5$$

(Schneider and Schütz, Ber. 1913, 46, 2634).

It gives cheirolin and glucose on hydrolysis (Schneider and Lohmann, Ber. 1912, 45, 2954).

Glucotropæolin $C_{14}H_{18}O_9NS_2K$, the glucoside of benzylthiocyanide, occurs in *Tropæolum majus* (Linn.). and *Lepidium sativum* (Linn.). It is known only in solution; with silver nitrate a precipitate is formed at first soluble in ammonia, but subsequently the ammonium compound



$$C\begin{array}{l}\diagup O{\cdot}SO_2{\cdot}OAg\\ \;SAg\\ \diagdown N{\cdot}CH_2Ph\end{array} + 2NH_3$$

separates in glistening crystals. The glucoside is hydrolysed by myrosin to glucose, potassium hydrogen sulphate, and benzyl*iso*thiocyanate (Gadamer, Ber. 1899, 32, 2336). *Nasturtium officinale* (R. Br.), and *Barbarea præcox* (R. Br.), are said to contain a glucoside, *gluconasturtiin*, which differs from glucotropæolin only in yielding phenylethyl*iso*thiocyanate $C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}NCS$ on hydrolysis by myrosin.

Glycyphyllin $C_{21}H_{24}O_9,3Aq$, m.p. 175°, occurs in the leaves of *Smilax glycyphylla* (Sm.); on hydrolysis it yields rhamnose and phloretin identical with that obtained from phloridzin, in which it is combined with glucose (Wright and Rennie, Chem. Soc. Trans. 1886, 49, 857).

Gossypitrin $C_{21}H_{20}O_{13}$, m.p. 200°–202°, occurs together with quercimeritrin and *iso*quercitrin in Egyptian cotton flowers, *Gossypium herbaceum* (Linn.). It consists of pale orange-yellow needles, gives a deep red precipitate with aqueous lead acetate, and an olive-green coloration with ferric chloride (Perkin, Chem. Soc. Trans. 1909, 2181). It is hydrolysed by boiling dilute sulphuric acid to glucose and gossypetin $C_{15}H_{10}O_8$, a hydroxyflavone derivative. The glucoside exists in the flowers as a potassium salt (A. G. Perkin, Chem. Soc. Trans. 1899, 75, 825; 1902, 81, 205; 1910, 95, 1855, 2181).

Gynocardin $C_{13}H_{19}O_9N,1\tfrac{1}{2}Aq$, m.p. 162°, $[\alpha]_D +72{\cdot}5°$, is found in *Gynocardia odorata* (R. Br.) and *Pangium edule* (Rein.), (Power and Lees, *ibid.* 1905, 87, 349; De Jong, Rec. trav. chim. 1909, 28, 24). It is hydrolysed by acids and by a specific enzyme gynocardase to glucose, hydrogen cyanide and a complex $C_6H_8O_4$, which spontaneously resinifies.

Helicin *v.* *Salicin.*

Helleborein is an amorphous glucoside, $[\alpha]_D -3°$, and yields on hydrolysis 1 molecule acetic acid, 2 molecules glucose, 2 molecules arabinose, and two *helleboretins*, one of which, $C_{21}H_{36}O_7$, is an acidic lactone, the other, $C_{18}H_{24}O_3$, being a neutral compound (Sieburg, Arch. Pharm. 1913, 251, 154).

Hesperidin $C_{50}H_{60}O_{27}$, m.p. 251°, $[\alpha]_D -89°$, is found generally in the fruit of the *Aurantiaceæ*. It was discovered in unripe oranges, and occurs in most species of *Citrus* except *C. decumana* (Murr.). It is a colourless, microcrystalline, tasteless, hygroscopic powder, almost insoluble in water, readily soluble in hot acetic acid. It is faintly acid, and therefore soluble in alkalis, from which it is precipitated by carbon dioxide. It is hydrolysed by acids to glucose (2 mols.), rhamnose, and (2 mols.) hesperitin $C_{16}H_{14}O_6$, which has the structure

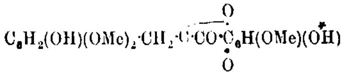
$$MeO\,C_6H_3(OH){\cdot}CH:CH{\cdot}CO{\cdot}O{\cdot}C_6H_3(OH)_2,$$

and is decomposed on boiling with alkali into phloroglucinol and hydroxymethoxycinnamic acid (Will, Ber. 1887, 20, 1186; Tiemann and Will, Ber. 1881, 14, 946).

Incarnatrin $C_{21}H_{20}O_{12},3Aq$, m.p. 242°, occurs in the flowers of *Trifolium incarnatum* (Linn.), the so-called 'carnation or crimson clover' (Rogerson, Chem. Soc. Trans. 1910, 1004), and forms faintly yellow prismatic needles. It is readily hydrolysed by acids and by emulsin to glucose and quercitin.

Indican $C_{14}H_{17}O_6N,3Aq$, m.p. 100° 102°, the glucoside of woad (*Isatis tinctoria* [Linn.]) is also found in *Indigofera tinctoria* (Linn.) and other species of *Indigofera*, in *Polygonum tinctorium* (Ait.), and in *Wrightia tinctoria* (R. Br.). It is conveniently extracted from the leaf by means of acetone. It is hydrolysed by acids, by a specific enzyme, *indemulsin*, present in the leaves of the indigo plant, and more slowly by the emulsin of almonds, to glucose and indoxyl. Indoxyl (colourless) undergoes oxidation to indigotin (blue) when exposed to the air $2C_8H_7ON + O_2 = 2H_2O + C_{16}H_{10}O_2N_2$. The yield of indigotin obtained from the leaves is of great importance commercially; it is below the theoretical when hydrolysis is slow, owing to the great instability of indoxyl, and in part to the occlusion of indoxyl by the enzyme. It is improved by adding a small quantity of sulphuric acid to the mixture at the commencement of the reaction (*see* Perkin and Bloxam, Chem. Soc. Trans. 1907, 91, 715; 1909, 95, 793, 824; also references to Indican given by Armstrong, The Simple Carbohydrates and Glucosides, London, 1919).

Iridin $C_{24}H_{26}O_{13}$, m.p. 208°, occurs in the root of the violet (*Iris florentina* [Linn.]) (De Laire and Tiemann, Ber. 1893, 26, 2010), and crystallises in colourless needles, very sparingly soluble. It is hydrolysed by acids to glucose and irigenin $C_{18}H_{16}O_8$, which has the constitution:



$$C_6H_2(OH)(OMe)_2{\cdot}CH_2{\cdot}\overset{\frown}{C{\cdot}CO{\cdot}}\underset{O}{\overset{O}{C_6}}H(OMe)(\overset{*}{O}H).$$

The sugar residue is attached to the hydroxyl marked *.

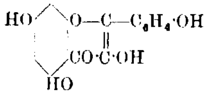
Jalapin (*Scammonin*) $C_{34}H_{56}O_{16}$, m.p. 131°, $[\alpha]_D -23°$, is the active principle of the root stalks of *Convolvulus orizabensis* (Led.), and of scammony, the dried sap of *Convolvulus scammonia* (Linn.). It is an amorphous resinous powder, translucent in thin plates; slightly soluble in water, readily soluble in alcohol and ether. It dissolves in concentrated sulphuric acid with a purple or maroon red colour, changing to brown and becoming finally black. It is hydrolysed by acids to glucose (3 mols.) and jalapinolic acid $C_{16}H_{30}O_3$, possibly hydroxyhexadecylic acid; this yields methylethylacetic acid, sebacic acid, and an isomeride of this acid on oxidation.

Jesterin $C_{26}H_{40}O_{13}$, m.p. 205°–218°, occurs in the berries of *Rhamnus cathartica* (Linn.). It is hydrolysed to a hexose, a pentose, and emodinanthranol $C_{15}H_{12}O_4$ (Krasowsky, J. Russ. Phys. Chem. Soc. 1908, 40, 1510).

Kaempferin $C_{27}H_{30}O_{16}$,6Aq is found in Senna leaves, melts at 185°–195°, and gives kaempferol and glucose on hydrolysis.

Glucosides of rhein and aloe-emodin are also present in Senna leaves (Tutin, Chem. Soc. Trans. 1913, 103, 2006).

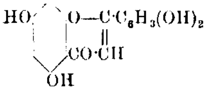
Kampferitrin $C_{27}H_{30}O_{14}$, m.p. 201°, is found in *Indigofera arrecta* (Hochst.) (Perkin, Chem. Soc. Trans. 1907, 91, 438), and forms almost colourless sparingly soluble needles; on hydrolysis rhamnose (2 mols.) and kampferol $C_{15}H_{10}O_6$ are formed—the latter has the constitution



Kampferitrin closely resembles robinin, which, according to Perkin, is also a glucoside of kampferol.

Linamarin (*Phaseolunatin*) $C_{10}H_{17}O_6N$, m.p. 141°, $[\alpha]_D$ 26°, found in *Phaseolus lunatus* (Linn.), the so-called Java beans, in flax, *Linum usitatissimum* (Linn.), and in cassava. It is hydrolysed by an enzyme, linase, present in *Phaseolus* and some *Linum* species, which is allied to but not identical with emulsin, and also by mineral acids, to glucose and acetonecyanohydrin. It is a derivative of β-glucose and not of α-glucose, as originally supposed (comp. Armstrong and Horton, Proc. Roy. Soc. 1910, B82, 349; Dunstan and Henry, *ibid.* 1903, 72, 285; 1906, B78, 145; 1907, B79, 315; Jorissen and Hairs, Bull. Akad. Roy. Belg. 1891, 21, 529).

Lotusin $C_{28}H_{31}O_{16}N$, obtained from *Lotus arabicus* (Linn.) (Dunstan and Henry, Phil. Trans. 1901, B, 194, 515), crystallises in pale yellow needles. It is hydrolysed by a specific enzyme, lotase, to glucose (2 mols.), hydrogen cyanide and lotoflavin, an isomeride of fisetin, which has the constitution



Apparently the hydrogen cyanide is attached to the sugar residue, as on alkaline hydrolysis heptagluconic acid is obtained.

Meliatin $C_{15}H_{22}O_9$, colourless, bitter crystals, m.p. 222°, occurs in the Marsh Trefoil (*Menyanthes trifoliata*). Upon hydrolysis with emulsin, glucose is produced (Bridel, Compt. rend. 1911, 152, 1694).

Morindin $C_{26}H_{28}O_{14}$ or $C_{27}H_{30}O_{15}$, m.p. 245°, found in *Morinda citrifolia* (Linn.), *M. tinctoria* (Roxb.), and *M. umbellata* (Linn.), crystallises in lustrous silky yellow needles, soluble in hot water and in alcohol. It dissolves in alkalis with an orange-red colour which is not changed on boiling, and in concentrated sulphuric acid with a purple-blue coloration. It is hydrolysed by acids to a sugar which has not yet been definitely identified, and morindone, a trihydroxymethylanthraquinone, isomeric with emodin. On distillation with zinc-dust, β-methylanthracene is formed. According to Perkin, morindin from *M. citrifolia* and *M. umbellata* is not the same (*see* Perkin and Hummel, Chem. Soc. Trans. 1894, 65, 851; Thorpe and Smith, *ibid.* 1868, 53, 171; Oesterle and Tisza, Arch. Pharm. 1907, 245, 534).

Myrticolorin *v. Rutin.*

Naringin, formula uncertain +4Aq, m.p. 170°, is found in the flowers and other parts only of the Java orange, *Citrus decumana* (Murr.). It forms colourless microscopic prisms of bitter taste, sparingly soluble in water, which are strongly lævo-rotatory. It dissolves in alkalis with a yellowish-red coloration and is precipitated by carbon dioxide. It is readily hydrolysed by acids to rhamnose and possibly also glucose and naringenin, which is the phloroglucinol ester of paracoumaric acid

$$C_6H_4(OH){\cdot}CH:CH{\cdot}CO{\cdot}O{\cdot}C_6H_3(OH)_2.$$

It is closely allied to hesperitin (comp. Will, Ber. 1887, 20, 297, 1186).

Osyritrin *v. Rutin.*

Phloridzin $C_{21}H_{24}O_{10}$,2Aq. m.p. 108° and again 170°, was discovered in 1835 in the bark and particularly the root bark of the apple, pear, cherry, and plum tree. It forms long silky needles of bitter taste, sparingly soluble in cold, readily in hot water; it is lævo-rotatory $[\alpha]_D$ −50°. Emulsin is without action, but acids hydrolyse it to glucose and phloretin

$$C_6H_2(OH)_3{\cdot}CO{\cdot}CHMe{\cdot}C_6H_4(OH)$$

(Rennie, Chem. Soc. Trans. 1887, 51, 636; Fischer, Ber. 1888, 21, 988). Glycyphyllin is the rhamnose ether of phloretin.

Phytosterolins. The following substances, believed to be phytosterols, were shown to be glucosides (phytosterolins) (Power and Salway, Trans. Chem. Soc. 1913, 103, 399):—

Substance.	*Found in:*	*M.P.*
Ipuranol	Olive bark, *Ipomoea Purpurea*, &c.	285°–290°
Citrullol	Colocynth, *Euonymus atropurpureus*, &c.	285°–290°
Bryanol	Bryony root	210°–212°
Cluytianol	*Taraxacum*	297°

Picein. Gluco-*p*-hydroxyacetophenone, synthesised by Mauthner in 1912, was shown by him to be identical with Tanret's picein, isolated from pine needles (J. pr. Chem., 1913 (ii.), 88, 764).

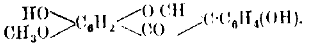
Polygonin $C_{21}H_{20}O_{10}$, m.p. 202°, from *Polygonum cuspidatum* (Sieb. and Zucc.), crystallises in lustrous yellow needles. It is hydrolysed by acids to glucose and emodin, identical with that obtained from frangulin, where it is combined with rhamnose (Perkin, Chem. Soc. Trans. 1895, 67, 1084).

Populin $C_{20}H_{22}O_8$,2Aq, m.p. 180°, has been found in the bark and leaves of *Populus tremula* (Linn.), *P. nigra* (Linn.), and *P. balsamifera* (Linn.), and other species of *Populus*. It is prepared synthetically from salicin by heating with benzoylchloride (Schiff, Annalen, 1870, 154, 5). It crystallises in minute needles, sparingly soluble in cold water, more soluble in hot water. It is lævo-rotatory, and dissolves in concentrated sulphuric acid with an amaranth-red coloration. Emulsin is without action, but acids hydrolyse it to glucose, saligenin, and benzoic acid. Nitric acid oxidises it to benzoyl helicin (Piria, *ibid.* 1852, 81, 245; 1855, 96, 375). This proves the benzoyl group to be in the sugar and not in place of the hydroxyl as often supposed. Populin is hydrolysed by the enzyme of *Populus monilifera* (Ait.) (Weevers, Proc. K. Akad. Wetensch. Amsterdam, 1909, 12, 193).

Prulaurasin $C_{14}H_{17}O_6N$, m.p. 122°, $[\alpha]_D$ $-52{\cdot}75°$, occurs in the leaves of the common cherry laurel, *Prunus laurocerasus* (Linn.) (Hérissey, Compt. rend. 1905, 141, 959).. It is hydrolysed by emulsin and by an enzyme prunase of the emulsin type, as also by mineral acids, to glucose, benzaldehyde, and hydrogen cyanide. It is the glucoside of racemic mandelonitrile, and in view of the fact that it is readily obtained from sambunigrin or from amygdonitrile glucoside by the action of traces of alkali (Caldwell and Courtauld, Chem. Soc. Trans. 1907, 91, 671), it is not impossible that it is present in the plant in one of these active forms, and undergoes racemisation during extraction.

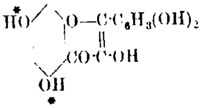
Prunasin *v. Amygdonitrile glucoside.*

Prunitrin $C_{22}H_{24}O_{11},4Aq$, found in the bark of *Prunus emarginata* (Walp.) (Finnemore, Pharm. J. 1910, 85, 604), is hydrolysed by acids to glucose and prunetin.



$$\begin{matrix}HO\\CH_3O\end{matrix}\Big> C_6H_2 \Big< \begin{matrix}O\cdot CH\\CO\end{matrix} \diagup C\cdot C_6H_4(OH).$$

Quercimeritrin $C_{21}H_{20}O_{12},3Aq$, m.p. 247°, obtained from the flowers of *Gossypium herbaceum* (Linn.), forms small glistening bright yellow plates, almost insoluble in cold and fairly readily soluble in boiling water (Perkin, Chem. Soc. Trans. 1909, 95, 2181). The alkaline solutions are deep yellow; it gives a bright-red precipitate with aqueous lead acetate. It is very stable towards mineral acids, but is eventually hydrolysed to glucose and quercetin. The glucoside exists in the flowers in a readily soluble condition in the form of a potassium salt. Quercimeritrin contains the quercetin hydroxyl groups in the 3′, 4′, and 3- positions intact, the sugar residue R being united to one of the hydroxyl groups marked *



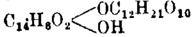
Quercitrin $C_{21}H_{20}O_{11},2Aq$, m.p. 183°–185°, or anhydrous 250°–252°, $[\alpha]_D-140{\cdot}9°$, found in the bark of *Quercus discolor* (Ait.) and elsewhere; crystallises in bright-yellow lustrous needles, almost insoluble in cold, sparingly soluble in hot water, and easily soluble in alcohol. It shows an intense green coloration with ferric chloride. Emulsin is without action, acids readily hydrolyse it to rhamnose and quercitin (tetrahydroxyflavonol). In quercitrin, the sugar group is not attached to the phloroglucinol residue, but to one or other of the three remaining hydroxyls (Hlasiwetz and Pfaundler, Ann. 1863, 127, 362; Liebermann and Hamburger, Ber. 1879, 12, 1178, &c.).

***iso*Quercitrin** $C_{21}H_{20}O_{12}$, m.p. 217°–219°, also found in the flowers of *Gossypium herbaceum* (Perkin, Chem. Soc. Trans. 1910, 95, 2181), crystallises in pale-yellow needles almost insoluble in cold and but sparingly in boiling water. With lead acetate it gives a bright-yellow precipitate, very different from the deep-red deposit produced from quercimeritrin. The glucoside is isomeric with quercimeritrin, and, like it, yields glucose and quercetin on hydrolysis, but differs in being readily attacked. The shades produced with the glucoside on mordanted wool closely resemble those yielded by quercitrin, but are entirely distinct from those given by quercimeritrin. The sugar is attached to either the 3′, 4′, or 3- positions, and not to the phloroglucinol nucleus.

Quinovin (*Chinovin*) $C_{30}H_{46}O_8$ or $C_{38}H_{62}O_{11}$, α-quinovin accompanies the cinchona alkaloids; it is obtained from the bark of *China nova*, which, after extraction with water, is boiled with milk of lime. The glucoside is precipitated on the addition of hydrochloric acid, and after purification forms a colourless crystalline powder, $[\alpha]_D$ $+59{\cdot}1°$: it is almost insoluble in water, and has a bitter taste. Alcoholic hydrogen chloride hydrolyses it to quinovaic acid $C_{24}H_{38}O_4$, and a methyl pentose, quinovose (*v.* CARBOHYDRATES), which, however, under these conditions, is converted into the glucoside ethylquinovoside (quinovite) $C_6H_{11}O_4{\cdot}OC_2H_5$. β-Quinovin is found in the *Remijia* species, and crystallises in plates, m.p. 235°, $[\alpha]_D+27{\cdot}9°$: it yields the same products on hydrolysis (compare Hlasiwetz, Ann. 1859, 111, 183; Rochleder, Zeitsch. Chem. 1867, 357).

Robinin $C_{33}H_{40}O_{19}$, the glucoside of the white azalea, *Robinia pseud-acacia* (Linn.), yields, on hydrolysis, galactose, rhamnose (2 mols.), and a yellow colouring matter robigenin $C_{15}H_{10}O_6$, closely related to quercetin (Schmidt, Arch. Pharm. 1904, 242, 210; Perkin, Chem. Soc. Trans. 1902, 81, 473).

Ruberythrinic acid $C_{26}H_{28}O_{14}$, m.p. 258°, is the constituent of madder root, *Rubia tinctorum* (Linn.), which, on hydrolysis, yields alizarin. It crystallises in citron-yellow needles, sparingly soluble in cold water. It dissolves in concentrated sulphuric acid, and in alkalis with a bright-red coloration. Acids and the enzymes of madder hydrolyse it to glucose (2 mols.) and alizarin (dihydroxyanthraquinone). Since the glucoside is acid, the two glucose molecules are probably united as a disaccharide, and not attached to both hydroxyl groups. The formula



$$C_{14}H_6O_2\Big<\begin{matrix}OC_{12}H_{21}O_{10}\\OH\end{matrix}$$

thus represents the glucoside (Liebermann and Bergami, Ber. 1887, 20, 2241; Schunck and Marchlewski, Chem. Soc. Trans. 1894, 65, 182).

Rubiadin glucoside $C_{21}H_{20}O_9$, m.p. 270°, also present in madder, forms yellow needles, which are hydrolysed to glucose and methyldihydroxyanthraquinone (Schunck and Marchlewski, Chem. Soc. Trans. 1893, 63, 969, 1137).

Rutin $C_{27}H_{30}O_{16},3Aq$, m.p. 184°, originally discovered in rue, *Ruta graveolens* (Linn.); also occurs in *Fagopyrum esculentum* (Moench), *Capparis spinosa* (Linn.), *Globularia Alypum* (Linn.), *Colpoon compressum* (Berg.), *Eucalyptus macrorhyncha* (F. Muell.), *Viola tricolor* (Linn.), *Tephrosia purpurea* (Pers.), &c.; it is identical with glucosides described as violaquercitrin, osyritrin, myrticolorin. It forms pale-yellow lustrous needles sparingly soluble in cold water and alcohol, more soluble on heating. It is hydrolysed with some difficulty to glucose, rhamnose, and quercitin (compare Schmidt, Arch. Pharm. 1904, 212, 210; 1908, 246, 214; Wunderlich, *ibid.* 1908, 246, 224, 241).

Sakuranin $C_{22}H_{24}O_{10}$,4Aq, m.p. 210°–212°, the glucoside of *Prunus paniculata* (Thunb.), the Japanese cherry tree, forms colourless bitter needles, and yields glucose and sakuranetin $C_{16}H_{14}O_5$, m.p. 150° on hydrolysis. It is physiologically inert. Sakuranetin contains one methoxyl group, absorbs bromine, and yields phloroglucinol, acetic, and *p*-hydroxybenzoic acids when fused with potash (Asahina, Arch. Pharm. 1908, 246, 259).

Salicin $C_{13}H_{18}O_7$, m.p. 201°, $[\alpha]_D -65°$, is the bitter stuff of willow bark, and was formerly used as a remedy against fever. It is found in many but not all *Salix* species, and besides the bark it occurs also in the leaves and female flowers. The amount varies according to the time of year It occurs also in poplars and in the flower buds of meadow-sweet, *Spiræa Ulmaria* (Linn.). It crystallises in needles, plates, or rhombic prisms. It dissolves in about 30 parts of cold water, easily in hot water. The solutions taste bitter and are lævo-rotatory. It dissolves in concentrated sulphuric acid with an intense red coloration: this is the so-called 'rutilin' reaction. Emulsin readily hydrolyses it to glucose and saligenin (*o*-hydroxybenzyl alcohol). It is also hydrolysed by a specific enzyme salicase present in willow leaves and twigs.

Benzoyl salicin is the natural glucoside *populin*. Mild oxidation with dilute nitric acid converts the primary alcohol group of salicin into aldehyde, forming *helicin* $C_{13}H_{16}O_7$; *e.g.*

$$C_6H_4(OC_6H_{11}O_5)CHO.$$

This forms bunches of slender needles, m.p. 174°. Emulsin hydrolyses it to glucose and salicylaldehyde. Helicin was synthesised by Michael by the interaction of acetochloroglucose and potassium salicylaldehyde.

Salinigrin $C_{13}H_{16}O_7$, m.p. 195°, $[\alpha]_D -87{\cdot}3°$, found only in *Salix discolor* (Muhl.) (Jowett and Potter, Pharm. J. Aug. 16, 1902), is the glucoside of *m*-hydroxybenzaldehyde, an isomeride of helicin. It gives no colour with sulphuric acid.

Sambunigrin $C_{14}H_{17}O_6N$, m.p. 151°, $[\alpha]_D -76°$, is present in the leaves of the elder, *Sambucus nigra* (Linn.). It is isomeric with amygdonitrile glucoside, although, like this, it is hydrolysed by emulsin, the products being glucose and *l*-mandelonitrile, *i.e.* the nitrile of *d*-mandelic acid (Bourquelot and Danjou, Compt. rend. 1905, 141, 59, 598).

Saponins $C_nH_{2n-8}O_{10}$ are a class of closely analogous glucosides, very widely distributed in plants, having the property of dissolving in water, giving clear solutions which froth strongly on agitation, form emulsions with oils and resinous substances, and prevent the deposition of finely divided precipitates. They have a bitter acrid taste, and the dust is very irritating and sternutatory; they are colloids and not dialysable. The more poisonous are distinguished as sapotoxins. They are hydrolysed by dilute acids to glucose, galactose, and active substances termed sapogenins: the different saponins give different proportions of sapogenin and sugar.

The sapogenins from many saponins, such as *Guaiacum*, *Saponaria*, *Senegin*, and *Digitonin* saponins, have been distilled with zinc dust in an atmosphere of hydrogen, and found to yield a mixture of terpenes including sesquiterpenes (van der Haar, Arch. Pharm. 1913, 251, 217).

Saponins are prepared by extraction with water and precipitation with neutral lead acetate, if acid saponins are present: basic lead acetate is then added to the filtrate to precipitate the neutral saponins. The precipitates are decomposed and the saponin solutions evaporated, the residue being purified by solution in chloroform and precipitation by ether. For further purification, the saponin is precipitated by barium hydroxide, and the barium compound decomposed by carbon dioxide.

Saponins form double compounds with cholesterol (*v.* *Digitonin*). The best-known saponins are:

Quillaic acid $C_{19}H_{30}O_{10}$, the acid glucoside obtained from the bark of *Quillaja Saponaria* (Molina), is a constituent of commercial saponin. The pure glucoside is non-poisonous: it forms white flakes, which become red on treatment with strong sulphuric acid.

Quillaia sapotoxin $C_{17}H_{26}O_{10}$, derived from the same source, is a colourless amorphous powder possessing poisonous properties.

Saporubrin $(C_{18}H_{28}O_{10})_4$, the sapotoxin from the root of the soapwort, *Saponaria officinalis* (Linn.), has $[\alpha]_D -54°$. It yields a series of sapogenins on hydrolysis, each giving up a further molecule of sugar as the treatment with dilute acid is continued. The final product has the formula $C_{14}H_{22}O_2$.

Levant sapotoxin $(C_{17}H_{26}O_{10},H_2O)_2$ from the root of *Gypsophila Arrostii* (Guss.) or *G. paniculata* (Linn.), is very similar to saporubrin. On hydrolysis, 4 mols. sugar (56 p.c.), probably a mixture of glucose and galactose, and a sapogenin $C_{10}H_{16}O_2$ (23 p.c.), are formed.

Agrostemma sapotoxin $(C_{17}H_{26}O_{10})_2$, from the corncockle, *Lychnis (Agrostemma) Githago* (Scop.), is a yellowish-white amorphous powder yielding 4 mols. sugar and a sapogenin $C_{10}H_{16}O_2$ on hydrolysis. It is absorbed by both the subcutaneous tissue and the intestines, and is therefore a dangerous poison.

Parillin $C_{26}H_{44}O_{10}$, one of the saponin glucosides of sarsaparilla, the dried root of various *smilax* species, has m.p. 177°, $[\alpha]_D -42°$. It is hydrolysed to a mixture of two sugars and parigenin $C_{28}H_{48}O_4$. The other glucosides of sarsaparilla are *smilasaponin* $(C_{20}H_{32}O_{10})_5$ and *sarasaponin* $(C_{22}H_{36}O_{10})_{12}$, m.p. 223°.

Sarsaparilla saponin, from *Smilax ornata* (Hooker), contains a *phytosterolin*, crystalline needles, m.p. 280°, $C_{33}H_{56}O_6$, and hydrolysing to glucose and *sitosterol*; and *sarsasaponin* $C_{44}H_{76}O_{20}$,7Aq, crystals, m.p. 248°. The latter yields on hydrolysis 3 mols. of glucose and 1 mol. of *sarsasapogenin* $C_{26}H_{41}O_2(OH)$,1½Aq, m.p. 183°, $[\alpha]_D -60°$.

The *smilacin* or *smilasaponin* of v. Schulz is not a homogeneous substance (Power and Salway, Chem. Soc. Trans. 1914, 105, 201).

Caulophyllosaponin $C_{66}H_{104}O_{17}$, m.p. 250°–260°, $[\alpha]_D +32°$, is a crystalline saponin found in *Caulophyllum thalictroides* (Linn.), which yields 2 mols. *l*-arabinose and 1 mol. *caulophyllosapogenin* $C_{56}H_{88}O_3(OH)_6$ (Power and Salway, Chem. Soc. Trans. 1913, 103, 191).

Caulosaponin $C_{54}H_{88}O_{17}$, m.p. 250°–255°, is a crystalline saponin found in *Caulophyllum thalictroides*, and gives 2 mols. glucose and 1 mol. *Caulosapogenin* $C_{42}H_{62}O_2(OH)_4$ upon hydrolysis (Power and Salway, Chem. Soc. Trans. 1913, 103, 191).

Digitosaponin is a colourless amorphous substance present with gitalin in *Digitalis* leaves, which gives *digitosapogenin* and a pentose on hydrolysis (Kraft, Arch. Pharm. 1912, 250, 118). It is apparently identical with Schmiedeburg's *digitonin*.

Hederins. The following saponins have been isolated from ivy (*Hedera helix*):—

a-Hederin $C_{42}H_{66}O_{11}$ (?), crystalline needles, m.p. 256°–257°, insoluble in water, and giving on hydrolysis arabinose, rhamnose, and *a*-hederogenin $C_{31}H_{50}O_4$, a dihydroxylactone melting at 325°-326°;

β-Hederin, a crystalline saponin insoluble in water;

γ-Hederin, an amorphous saponin insoluble in water; and

Δ-Hederins, a mixture of saponins soluble in water (van der Haar, Biochem. Zeitsch. 1916, 76, 335).

Polysciasaponins, from *Polyscias nodosa*, are white amorphous products, carbonising at about 325°.

On hydrolysis with 5 p.c. sulphuric acid, equimolecular amounts of arabinose, glucose, and a *sapogenin* $C_{26}H_{44}O_4$ are produced; the latter forms rhombic crystals, m.p. 324°, and is a saturated lactone, but contains no carboxyl, hydroxyl, methoxyl, or ethoxyl groups (van der Haar, Biochem. Zeitsch. 1916, 76, 335).

Prosapogenin, from *Gypsophila* saponin and dilute sulphuric acid, melts at 207°, and with 2 p.c. sulphuric acid under pressure gives a *sapogenin* $C_{24}H_{34}O_5$, m.p. 267°, a monobasic ketonic acid (Rosenthaler and Ström, Arch. Pharm. 1912, 250, 290).

Saponarin from *Saponaria officinalis.* The aqueous solution of the crystalline saponin is not coloured by iodine, but the colloidal aqueous solution gives a blue adsorption compound with this reagent (Barger and Field, Chem. Soc. Trans. 1912, 101, 1394).

Saponin from *Sapindus Makurosi*, an amorphous white powder, $[\alpha]_D+13°$, hydrolysing to *d*-arabinose and a crystalline *sapogenin*, m.p. 310° (Asahina and Shimidzu, J. Pharm. Chim. 1916, [vii.] 14, 188).

Saponin from *Styrax japonica*, a crystalline calcium salt, m.p. 254°–257°. Treatment with 0·5 p.c. hydrochloric acid gives the free saponin, *jegosaponin* $C_{55}H_{80}O_{25}$, m.p. 238°, $[\alpha]_D-39°$. This hydrolyses to glucose, glycuronic and tiglic acids, and a mixture of *sapogenins* (α- $C_{33}H_{52}O_6$, m.p. 150°, and β- $C_{33}H_{52}O_7$, m.p. 225°–228°) (Asahina and Momoya, Arch. Pharm. 1914, 252, 56).

Saponin from *Yucca angustifolia* (root-stock) $C_{36}H_{58}O_{20}$, gives galactose on hydrolysis (Viehoever, Chernoff, and Johns, J. Biol. Chem. 1916, 24).

Saponin from *Yucca radiosa* (root-stem) $C_{27}H_{44}O_{20}$, gives glucose or mannose on hydrolysis (Johns, Geiger, and Viehoever, J. Biol. Chem. 1916, 24).

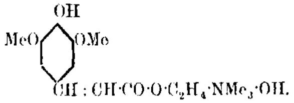
Scopolin $C_{22}H_{28}O_{14}$,2Aq, m.p. 218°, occurs in *Scopolia japonica* (Maxim.) and *S. carniolica* (Jacq.). It is hydrolysed to glucose (2 mols.) and scopoletin, which is identical with æsculin methyl ether (Eykman, Rec. trav. chim. 1884, 3, 177).

Serotin $C_{21}H_{20}O_{12}$,3Aq, m.p. 245°, found in the leaves of *Prunus serotina* (Ehrh.), commonly known as the wild black cherry, crystallises in golden yellow leaflets. It is more soluble in water and more readily hydrolysed than quercimeritrin. Acids convert it into glucose and quercitin (Power and Moore, Chem. Soc. Trans. 1910, 97, 1099).

Sinalbin $C_{30}H_{42}O_{15}N_2S_2$,5Aq, m.p. 138°–140°, found in white mustard *Sinapis alba* (Linn.), crystallises in faintly yellow-coloured needles which are slightly soluble in cold, easily soluble in hot water, and lævo-rotatory. It is hydrolysed by the myrosin present in the seeds to glucose, sinalbin mustard oil $C_7H_7O{\cdot}NCS$, and acid sinapin sulphate $C_{16}H_{24}O_5N{\cdot}HSO_4$. Sinapin $C_{16}H_{25}O_6N$ is only known in the form of its salts, barium hydroxide converts it into choline $C_2H_4(OH)N(OH)Me_3$ and sinapinic acid

$$C_6H_2(OH)(OMe)_2CH : CH{\cdot}CO_2H.$$

The alcohol corresponding to this acid is syringenin obtained from the glucoside syringin. Sinapin is accordingly



Sinalbin mustard oil has the composition

$$C_6H_4(OH){\cdot}CH_2{\cdot}N : CS.$$

Sinigrin $C_{10}H_{16}O_9NS_2K$,Aq, m.p. 126°, is the active principle of black mustard, *Brassica nigra* (Koch). It crystallises in lustrous colourless needles, very soluble in water, sparingly soluble in cold alcohol. It is lævo-rotatory. Myrosin or a water extract of the seeds hydrolyses it to glucose, allyl*iso*thiocyanate and potassium hydrogen sulphate. Emulsin is without action. As hydrolysis by myrosin proceeds, the increasing quantity of acid potassium sulphate formed renders the ferment less active and ultimately stops its action. Gadamer has proposed the formula, $C_3H_5N : C(SC_6H_{11}O_5)O(SO_2K)$. This is supported by Schneider and Wrede (Ber. 1914, 47, 2225), who found that the silver salt of thioglucose was produced by treatment of sinigrin with potassium methoxide followed by the action of ammoniacal silver nitrate.

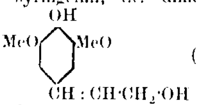
Skimmin $C_{15}H_{16}O_8$, m.p. 210°, occurs in *Skimmia japonica* (Thunb.). It crystallises in colourless needles, sparingly soluble in water, and dissolves in alkalis with a blue fluorescence. Acids hydrolyse it to glucose (?) and skimmetin ($C_9H_6O_3$), m.p. 223°, which is perhaps identical with umbelliferone (monohydroxycoumarin) (Eykman, Rec. trav. chim. 1884, 3, 208).

Solacein, a nitrogenous glucoside occurring in *Dulcamara* species, m.p. 236°–237°, hydrolyses to solanidine and a sugar (G. Masson, Bull. Sci. Pharm. 1912, 19, 283).

Solanine $(C_{27}H_{49}O_9N)_2,H_2O$, found in *Solanum sodomæum*, yields on hydrolysis galactose, a methylpentose, and the base solanidine $C_{18}H_{31}ON$, the constitution of which has not been determined, except that it is known to contain hydroxyl and imino groups.

Several different glucosides appear to have received the same name (Oddo and Cesaris, Gazz. chim. ital. 1911, 41, 490, 534; 1914, 44, [ii.] 181), *e.g. Solanine*, occurring in *Solanum angustifolium*, isolated by Tutin and Clewer (Trans. Chem. Soc. 1914, 105, 559); and *Solanine-s* $C_{54}H_{96}O_{18}N_2,H_2O$, occurring in *Solanum sodomæum*, which is hydrolysed to 1 mol. glucose, 1 mol. *d*-aldomethylpentose, 1 mol. *d*-galactose, and 2 mols. of solanidine-s $C_{18}H_{31}ON$, a base containing hydroxyl and imino groups (Oddo and Cesaris, Gazz. chim. ital. 1914, 44, [ii.] 181).

Strophanthin $C_{40}H_{66}O_{19}$, m.p. 170°–172°, is obtained from the seeds of *Strophanthus Kombe* (Oliver) and other species. It occurs as a pale-yellow amorphous or a colourless microcrystalline powder, having an intensely bitter taste and a faintly acid reaction. It is freely soluble in water and very poisonous. With concentrated sulphuric acid it is coloured green or orange, then red, and, on warming, dark-brown and finally green. Acids hydrolyse it to strophantidine $C_{27}H_{38}O_7$, and methyl strophantobioside $C_{13}H_{24}O_{10}$, which is in turn broken down to rhamnose, mannose, and methyl alcohol. Strophantin is similar to digitalis in its action on the heart.

Syringin $C_{17}H_{24}O_9$,1Aq, m.p. 191°, $[a]_D$ −17°, is found in the syringa, *Syringa vulgaris* (Linn.), and also in the bark of lilac and privet. It crystallises in slender needles, gives a reddish-violet coloration with sulphuric acid, and is readily soluble in warm water. It is hydrolysed by emulsin and by acids to glucose and syringenin, *i.e.* dimethoxyconiferyl alcohol 

(*see* Körner, Gazz. chim. ital. 1888, 18, 209).

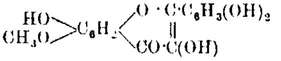
Trifolin $C_{22}H_{22}O_{11}$,1Aq, m.p. 260°, found in the flowers of the common red clover, *Trifolium pratense* (Linn.), forms slender pale-yellow needles. It gives intense yellow solutions with alkalis, gives a yellow solution which develops a green fluorescence in concentrated sulphuric acid. It is hydrolysed by acids to rhamnose and trifolitin $C_{16}H_{10}O_6$, a yellow colouring matter (Power and Salway, Chem. Soc. Trans. 1910, 97, 231).

Turpethin $C_{34}H_{56}O_{16}$, m.p. 149°, from the dried sap or root of *Ipomæa Turpethum* (R. Br.), is very similar to jalapin, but differs in being insoluble in ether. It is an amorphous powder. Acids hydrolyse it to glucose (3 mols.), turpethol $C_{16}H_{30}O_3$, *iso*butyric acid, and a viscid acid, $C_{15}H_{28}O_5$ (*see* Spirgatis, Annalen, 1866, 139, 41; and Kromer, Chem. Soc. Abstr. 1893, i. 482). Votoček and Kastner (Chem. Soc. Abstr. 1907, i. 330) have isolated two other glucosides, α- and β-turpethein from *I. turpethum*. The α-isomeride gives rhamnose, the β-isomeride rhodeose, and glucose when hydrolysed.

Vicianin $C_{19}H_{25}O_{10}N$, m.p. 160°, $[a]_D$ −20°, occurs in the seeds of *Vicia angustifolia* (Bertrand and Weisweiler, Compt. rend. 1908, 147, 252; 1910, 151, 325, 884). It is hydrolysed by an enzyme present in many *Vicia* species to *d*-mandelonitrile and a C_{11} disaccharide (vicianose), which is composed of glucose and arabinose. Vicianin therefore represents an amygdalin in which arabinose is substituted for glucose.

Violaquercitrin *v. Rutin.*

Xanthorhamnin $C_{34}H_{42}O_{20}$ is found in the fruits of *Rhamnus infectoria* (Linn.), *Rh. tinctoria* (Wald. and Kit.), and in various parts of other species of *Rhamnus*. It crystallises from alcohol in golden-yellow microscopic needles, is readily soluble in water and dissolves in alkalis with a yellow coloration. It is hydrolysed by an enzyme *rhamninase* to a trisaccharide (rhamninose) and rhamnetin $C_{16}H_{12}O_7$. Rhamninose is further hydrolysed by acids to rhamnose (2 mols.) and galactose. Rhamnetin is quercitin monomethyl ether



$$\begin{matrix}HO\\CH_3O\end{matrix}\!\!>C_6H_2<\!\!\begin{matrix}O\cdot C\cdot C_6H_3(OH)_2\\ \| \\ CO\cdot C(OH)\end{matrix}$$

(*see* Tanret, Compt. rend. 1899, 129, 725).

E. F. A.

GLUCURONIC ACID *v* CARBOHYDRATES.

GLUE AND GLUE TESTING. The term *glue* comprises preparations obtained by the action of water from certain portions of animals and fishes, which have the power of gelatinising in aqueous solution and drying up to a hard strongly adhesive layer.

Other preparations which possess this adhesive property are also loosely termed glues; *e.g.* marine glue, a resinous composition; gluten and casein glues, mineral and vegetable glues, &c., but, strictly speaking, they have no claim to that name, as they contain no gelatin.

The term *gelatin* is applied to glues made from specially selected stock, and so gelatin may be considered a purer form of glue.

Glue or gelatin is probably not contained as such in the animal, but is the product of the hydrolysis of various nitrogenous tissues, brought about by boiling with water.

These tissues have been classed as follows:—

(1) *Ossein*, of bones and skin, *Chondrigen*, of cartilage; *Isinglass*, from the bladders of fish; these are classed under the general name of *Collagens*.

(2) *Elastin*, from certain ligaments.

(3) *Chitin*, from beetles, locusts, shrimps, crabs, &c. It can be converted into a gelatinous form by treatment with acids, but is of no utility.

(4) *Keratin*, from hair, horns, hoofs, and feathers. These yield products which have little power of gelatinising, and are not used in the glue manufacture.

For convenience the products obtained from collagens by the action of water may be classed into Glutin and Chondrin, the properties of which will be described later.

Manufacture.—(*a*) **Bone glue.** For this purpose, bones of all kinds are used, and vary, therefore, so much in composition that it is useless to give any detailed analysis. In addition to calcium phosphate and carbonate, the main ingredients of the ash, they contain fat and gelatin-forming substances, ossein and chondrin. Before the gelatin can be obtained, it is necessary to remove the fat of which fresh bones such as ribs, heads, shoulder blades, contain from 12 to 13 p.c., while large thigh bones may contain 17 to 18 p.c. Marine store bones, such as have been used for soup, Indian and South American bones rarely contain more than 12 p.c. of fat.

There are in use three chief methods of extracting the fat :—

(1) By simply heating the bones in a tank provided with a steam coil ; (2) by heating with steam in a digestor under pressure ; (3) extraction of the fat by volatile solvents.

By the first of these processes, the yield is only about 10 p.c., by the second up to 12 p.c., whilst by the third almost all the fat can be obtained.

The solvent extraction process is the one now used in most modern factories. The solvents are mainly those portions of Scotch shale naphtha or American or Russian petroleum boiling from 90° to 105°, and coal-tar naphtha of similar boiling-point. In this country, Scotch shale naphtha, boiling between 100° and 115°, is usually employed. A modern extracting plant consists of, say, 6 cylindrical vertical boilers of a capacity of 5 tons of bones, worked in sets of three, one lot extracting while the other set is being emptied. As the bones are delivered at the works, they are sorted and then crushed in a mill and filled into the extractors, which are provided with perforated false bottoms, under which are placed wet and dry steam coils. At the top of each is a pipe for conveying off the vapour of the solvent to a set of condensers usually placed outside the building. When the extractors have been filled and the manholes closed, the solvent is run in and heat applied by the dry coils until the solvent begins to distil over, carrying with it the moisture present in the bones. When it begins to pass over free from moisture, the dry coils are shut off, and the first charge of the extracted fat run off from below the bones into the *mont-jus* or 'distiller.' This operation is repeated three or four times, when the bones are free from fat, but retain a considerable amount of the solvent, which is blown over by high-pressure steam from the wet coils into the condenser. The whole operation takes about 12 hours. The bones are then raked out through the lower manhole and conveyed to the cleanser. When dry, they should be free from smell, and contain not more than ¼ p.c. of fat. The fat held in solution in the solvent is then heated in the distiller to expel the solvent which is condensed and used again. The fat is freed from dirt by heating with hot water and settling, and is then run into barrels. It contains about 98 p.c. of pure fat and is used in soap, candle, glycerol, and in the case of fresh bones for margarine making.

The cleansing of the bones is done by passing them through a rotating cylindrical wire gauze sifter, and they are then ready for the boiling operation.

The extraction or 'cooking' is carried out in one of two ways : (1) By the alternate action of steam and water playing on the bones contained in a large iron boiler of from 3 to 5 tons capacity. As this method yields weak glue solutions, costly to concentrate, modern manufacturers prefer the second plan (2) *i.e.* to 'cook' in autoclaves under, say, 15 lbs. steam pressure, reduced later to 4 to 5 lbs., this being done to allow the glue contained in the interior of the bones to exude, so that it may be washed down by the spray of water. This action is repeated until the solution contains about 20 p.c. of glue.

The glue liquors are then clarified by standing in tanks, kept warm by steam coils, when the dirt settles, and any grease rising is skimmed off. To assist in the clarification, many substances have been suggested, such as blood, basic lead acetate, milk of lime, sodium phosphate, oxalic acid, albumen, but they are rarely used, as ½ p.c. of potash alum fulfils the purpose better than any of them. After adding the dissolved alum, the whole mass is agitated and heated to 80°, and then strained through fine wire gauze or canvas.

The glue solution, thus clarified, is then introduced into the concentrators, where excess of water is removed under reduced pressure, so as to avoid injury to the glue by heating to too high a temperature.

The principle of these concentrators is that of the vacuum pan, and the Yaryan type is one of the most modern forms.

This consists of an iron vessel, globular or cylindrical in shape, steam jacketed and provided internally with steam coils immersed in the glue solution. The dome, which is provided with baffle plates, is connected with a vacuum pump and condenser. In order to save fuel, the steam from the glue of one pan is led on the multiple-effect principle, into the coils and jacket of another, and so on to a third. (*V.* EVAPORATION.)

After concentration, the glue liquors, before settling, are usually bleached by the action of sulphur dioxide, produced in any suitable way, which is led through the liquors by perforated pipes while they are contained in lead-lined tanks and kept liquid by steam coils. When the required shade has been reached, the liquors are ready for jellying, and are run out into galvanised iron troughs, 2 feet × 6 inches, to the depth of 5 inches, and allowed to cool. When set, the mass is removed and cut by a 'wire knife' into sheets of suitable thickness. Or the troughs may be dispensed with and the liquid jellied on water-cooled glass slabs placed in rows on tables.

The drying operation, which follows, is one of the most important parts of the manufacture of glue. Since the jelly melts at a temperature of about 25° in summer, the air entering the drying rooms must be cooled, while in winter it is usually so charged with moisture that, in order to effect any desiccation of the jelly it must be warmed. These operations are carried out by suitable refrigerators and steam pipes.

The cakes of glue are placed on frames covered with nets, which may be of cotton or wire. These are supported on suitable trollies and placed in chambers through which air, of the proper temperature and humidity, as indicated by wet-and-dry bulb thermometers, is circulated by fans. In 4 or 5 days, the cakes are removed from the racks and packed ; they then contain 10 to 13 p.c. of water.

Osseine is a French preparation obtained by treating the fat-freed bones with dilute mineral acids, when the phosphates and other soluble salts are removed.

The residue consists of the glue-forming ingredients of the bones, and may be made into glue by treatment with water under heat, but in the writer's experience, the change is very slow, and the preparation, although useful to the manufacturer of glue, is not to be recommended to the ordinary consumer of size.

Hide or Skin glue. While the *epidermis* of the hide yields little or no glue, the *corium*, or inner skin, consisting mainly of connective tissue, gives a good percentage on treatment with hot water.

The raw materials for skin glue are the various clippings of hides, the ears and tails of oxen and sheep, rabbit and hare skins, old parchment, old gloves, pigs' skins, and all waste leather which has not been tanned.

The first process in the manufacture of glue from these is to subject them to the action of milk of lime in shallow pans or pits for several days, the skins being constantly stirred with forks.

These operations loosen the hair. From the pits, the skins are taken to the unhairing room, where the still adhering hair is scraped off by a blunt knife, and any fleshy parts, &c., removed. The hair thus obtained finds use in plastering work and felt making, &c.

Tanned leather cannot be used, but tannery waste trimmings, after the liming or depilatory process, form the raw material for good glue.

In modern practice, besides milk of lime, other substances, such as sodium sulphide, soda, and a mixture of soda and lime are used. The first is said to be good, but in presence of iron causes blackening of the hides.

After liming, the skins, when firm and free from greasy feel, are washed, first with water, then with dilute hydrochloric acid, and finally again with water. The excess of water is removed from the wet stock by drying and pressing.

The dried material is then heated, enclosed in sacks in a boiler with water until the liquors contain about 32 p.c. of glue. It may then be run in a Yaryan concentrator, or direct into coolers, or on to glass slabs for jellying and cutting and dried as before.

Fish glue. The raw materials for this are chiefly the skins (especially those of soles and plaice), the bladders of various fish and all varieties of fish offal. These yield, by processes similar to the above, a very adhesive but evil-smelling glue, which it is said may be deodorised by treatment with 1 p.c. of sodium phosphate and 0·25 p.c. of saccharine (Lambert).

Isinglass is a valuable product obtained from the swimming bladders of various fish, of which the sturgeon of the Volga yields the best quality, but Brazilian, Penang, Indian, and Hudson's Bay isinglass are also on the market. It arrives in this country either as the unopened bladders, known as pipe isinglass, or as purse, lump, or leaf, In preparing the last two, the bladders are cleansed by washing with hot water, and then cut open and dried.

Before solution in water, the crude isinglass is moistened, cut into strips, rolled out into ribbons and dried. When dry they are shredded by suitable machines. Isinglass is mainly used in clarifying wines, ciders, and beers, by the cook for making jellies, and in the preparation of plasters.

Glue size may be considered as a by-product, since it usually consists of the crude glue liquors which are the product of the third or fourth extraction of the raw material, which, if dried, would yield a glue of inferior quality. In small works and in some factories, where size is used, it is often made direct from bones or such leather waste as 'pickers' by treatment with lime, heating and straining.

Size is usually treated with sulphur dioxide to improve its colour and its keeping power. Zinc sulphate or boracic acid is often added as a preservative, and when sold it usually contains about from 25 to 38 p.c. of glue.

Concentrated size consists of ground glue, such cakes as are off shade and quality being used.

Coloured or Opaque glues are made by the addition of a small quantity of some pigment such as finely ground chalk or whitening.

Chemistry and Properties of Glue.

The products yielded by the hydrolysis of collagens may be divided into three groups :

(1) **Glutin (gelatin).** This is a colourless, yellowish, transparent, odourless, and tasteless body. It has the following composition :—

Gelatins from Connective Tissue.
(Chittenden, 1908.)

	1	2
Carbon	50·12	50·00
Hydrogen	6·68	6·52
Nitrogen	17·84	17·88
Sulphur	0·32	0·23
Oxygen	25·10	25·35
Ash	0·32	0·36

The quantity of sulphur varies considerably, and appears to be largely a constituent of the ash, which, in commercial glue, is often as high as 1·75 p.c. By precipitation with alcohol from aqueous solution, gelatin may be obtained almost ash- and sulphur-free. When immersed in water, glutin, while insoluble in the cold, swells up and greatly increases (5 or 6 times) in weight. It dissolves in hot water, and the solution, on cooling, sets to a jelly. Prolonged heating with water lessens its gelatinising power. Solutions of glutin on exposure to air rapidly putrefy, evolving, among other products, ammonia. It is insoluble in ether and alcohol, but soluble in glacial acetic acid (such solutions being made use of in the familiar 'Diamond cement' and 'Seccotine'). Solutions of glutin are not precipitated by gold, silver, or copper salts, but the two former are reduced to the metallic state on heating. Platinum salts give brown precipitates and form a delicate test for glutin. The various tannic acids precipitate glutin, with the production of leather-like substances. This precipitate is insoluble in organic solvents, such as ether and alcohol, but soluble in warm alkalis. Iron, aluminium, potassium, and lead salts cause no precipitate, but mercuric chloride renders its solution turbid. Chromium salts, especially potassium dichromate and chrome alum, have the power of rendering gelatin insoluhle in water after exposure to light, which property is made use of in photography and other industries.

Dry distillation of glutin yields water and a dark thick oil, similar to Dippel's oil, containing pyridene bases, aniline, &c. Formaldehyde, when added to a glutin solution, solidifies it and renders it no longer soluble even in hot water. 8 p.c. of formaldehyde on the dry glue gives maximum effect. This property has been utilised in waterproofing and in the production of Vandura silk.

(2) **Chondrin.** This horny substance, very similar to glutin, is contained in most glues, but differs in being precipitated from its solutions by nearly all acids, though usually soluble in excess. Many salts, such as alum, lead acetate, and iron salts, also precipitate it. Its composition is given as:

Carbon	49·92
Hydrogen	6·76
Nitrogen	15·65
Oxygen	27·67

Its gelatinising and adhesive powers are weaker than those of glutin.

(3) **Mucin.** This name covers a number of bodies which are usually removed in the liming operation. If left in the glue, they give rise to 'foaming,' and have little or no adhesive property.

Uses of glue.—A great variety of industries employ glue in some form or other. It is employed in sizing textiles, papers, walls, canvas, &c. It is also largely employed in joiners' work, veneering, box making, the making of matches, &c.

Mixed with glycerin, treacle, or glucose, it forms the compositions used as substitutes for rubber and for printing rollers, stamps, &c. Mixed with treacle or glycerin, it is employed in making the familiar 'jellygraph.'

It is also used in photography, and as gelatin it forms part of the raw materials of cookery.

Glue Testing.

The testing of glue has relation to the properties required for the particular purpose to which the glue is to be put. General requirements are tenacity, adhesiveness, and keeping power.

Chemical tests. (1) *Moisture determination.*—The sample of glue is reduced to shavings by means of a 'spoke-shave,' and these are ground to powder in a mortar. Five grams are weighed out on to a clock-glass and dried, first in the water-oven and then in a toluene bath to constant weight. Glues in this way yield 12 to 18 p.c. of moisture. A very low result is not desirable, as it shows the glue has been over-dried and has little tenacity, while a high result throws doubts on its keeping quality.

(2) *Ash.*—A portion of the glue is incinerated in a platinum crucible, and the ash weighed. That from bone glue fuses and gives, when taken up in dilute nitric acid, the phosphoric acid reaction with ammonium molybdate, whereas the ash from hide glue does neither, and is usually alkaline from the lime used in the preparation. The ash content of good glues varies from 1·5 to 3·0 p.c. Glues weighted with barytes, &c., and 'coloured glues,' of course, yield more.

(3) **Acidity** may be determined directly by titrating a measured quantity of, say, a 10 p.c. solution with standard alkali, using phenolphthalein as indicator. Should the glue solution be highly coloured, as is the case with some Scotch glues, fluorescein may be used in its place. The volatile acids of glue may be determined by dissolving 50 grams of the sample in water, and subjecting the solution to steam distillation. The steam and vapour are led through a condenser and received in a vessel containing a known volume of standard alkali. After some 300 c.c. have been condensed, the amount of acid absorbed by the alkali is determined by titration. It is expressed as H_2SO_3, and a good glue should not yield more than 0·2 p.c. (Lambert.)

(4) **Fatty matters** are determined by extracting 5 grams of the finely powdered sample, contained in a capsule in the Soxhlet apparatus with ether.

(5) **Determination of the gelatin content by yield of nitrogen.** Trotman and Hackford (J. Soc. Chem. Ind. 1904, 1072) give a process for the determination of the gelatin present in glue. They point out that a direct determination of nitrogen by Kjeldahl's method or soda lime distillation gives misleading results—owing to the presence of peptones, &c. (the decomposition products of gelatin) when it is multiplied by the factor 5·33. They consequently precipitate the gelatin with zinc sulphate crystals, wash the precipitate with concentrated zinc sulphate solution, and treat the product by the Kjeldahl process. The amount of nitrogen, multiplied by 5·33, gives the gelatin content. This method has been criticised by H. J. Wilson, but it appears to differentiate between gelatin and the other nitrogenous ingredients of glue.

Estimation by precipitation with tannic acid. Standard solutions of pure gelatin (10 grams per litre) and of tannic acid (10 grams per litre) are made. The two are then titrated together until no further precipitate is produced. A weighed quantity of the sample is then titrated against the tannic acid, and thus its gelatin content determined.

Stelling's method of determining gelatin consists in precipitating the solution by 96 p.c. alcohol, but owing to the partial solubility of gelatin in that menstruum, Rideal considers it untrustworthy.

(6) **Water absorption.** A very general method of testing glue consists in determining the amount of water which it will absorb. A weighed quantity of glue is covered with water at 60°F. (15·5°C.) and allowed to soak for from 24 to 48 hours, according to the thickness of the cake, or until the cake is thoroughly saturated by the water, which can be judged by its colour and appearance.

The cake is then removed, dried superficially with filter paper, and the increase of weight determined. Generally speaking, the greater the increase the better the glue, provided that the cake remains firm. Fine bone and skin glues will increase in weight 8 to 11 times, common glues 5 times, but some of the very common fish glues may liquefy completely under these conditions. In making this test, the smell of the glue and the colour of the water should be noted, when valuable information as to the keeping qualities and probable sources of the glue may be gleaned.

Jelly tests. 10 grams of glue are soaked for

24 hours in water, and then melted and the solution made up to 100 c.c. The solution is cooled, and the strength of the jelly tested with the finger. It is quite possible to grade the various samples of glue with considerable accuracy by this method.

Lipowitz shot test. If it is desired to have a quantitative expression of the strengths of the jellies yielded by a number of samples of glue, the samples containing 10 p.c. of glue may be run into cylinders of uniform width and allowed to set. The cylinders are then in turn covered with a lid, through which, in a guide tube, passes a stout wire, to the lower end of which is soldered a convex disc, while the upper end carries a pan to carry weights or shot. The convex surface of the disc rests on the surface of the jelly, and weights or shot are added to the upper pan until the lower disc penetrates. The greater the amount of weight the jelly will carry, the greater is its consistency.

This method is largely employed, but its value is only comparative.

Strength of jelly. The writer has used a method for some years which he claims to give more reliable results. 30 grams of glue are soaked in water and, after melting, the solution is made up to 100 c.c. and transferred to a vessel so that the depth of the layer is $1\frac{1}{2}$ to 2 inches. This, of course, may be varied according to the vessels at command, but it should be the same for all the samples. While the solution is still warm, a circular disc of metal 1 inch in diameter, to the centre of which is fixed a stout wire, is inserted. Halfpennies form convenient discs. The wire is kept in a vertical position until the solution has jellied. The vessel is clamped down and the wire attached to one arm of a stout balance. Weights are then placed in the other pan until the disc is torn through the jelly. The greater this weight, the tougher the jelly and stronger the glue. The test should be repeated several times, and the mean taken. A good glue under these conditions requires over 10 lbs. to tear the disc through the jelly. It is claimed that, by this method the variations due to the surfaces of the glue jellies are obviated.

Hulbert (J. Ind. Eng. Chem. 1913, 5, 235) has described a simple apparatus for testing the jelly-strength of glues (*cf.* Clark and Du Bois, J. Ind. Eng. Chem. 1918, 10, 707).

Melting-point of jelly. 15 grams of the sample are soaked in 30 c.c. of water for 12 hours, heated on the water-bath, and the solution poured into a wide test-tube in which a thermometer is inserted. In a similar tube, a solution of a good hide glue (1 : 1) is poured, and both tubes are immersed in water at 15°. When set, the two tubes are placed in a horizontal position on a shelf over a water-bath. Their melting-point is taken to be the temperature at which the surfaces of the glue solutions leave their vertical positions (Kissling).

According to Sammet (J. Ind. Eng. Chem 1918, 10, 595), comparison with standard glues shows that the melting-point may be taken as a measure of the jelly-strength.

Viscosity of jelly. Fels (J. Soc. Chem. Ind. 1901, 130) recommends that the viscosity of a 15 p.c. solution of glue at 30° should be tested in the Engler viscosimeter, on the assumption that the greater the viscosity the stronger is the glue.

Rideal uses a modified form of the Slotte instrument (J. Soc. Chem. Ind. 1891, 615), and uses 1 p.c. solutions at 18°.

A simple way of carrying it out is to run the solution from a burette; the time taken for 50 c.c. to flow is taken as a measure of its viscosity. Supposing 25 secs. are taken by water at that temperature, a 1 p.c. solution of a strong glue will take 32–34 secs.; a medium glue, 28–30 secs.; weak glues, 26–27 secs.

Tensile strength of glue. Many methods have been suggested such as Bauschinger's, Kissling's, and Rideal's. Rideal has devised the following method:—

Two plane surfaces of biscuit porcelain, ground so as to fit, 1 square inch in area, are soaked with a solution made up of 1 part of glue in 2 parts of water at 70° for 30 minutes; they are placed together, weighted with 5 lbs., and kept for 5 days in a cool room. They are then fixed in a testing machine, and the weight necessary to tear them asunder is determined (*cf.* Gill, J. Soc. Chem. Ind. 1915, 292).

The writer has used with success a slightly modified form of a method originally suggested by Millar (J. Soc. Chem. Ind. 1899, 16). 10 p.c. solutions of the glues to be tested are made up. Strips of filter or other paper are cut, 1 inch in width and about 18 inches in length. These are dipped in the solution at about 50°, and then hung up to dry. When the first coat has dried, they are again immersed in the solution and allowed to dry, the portion that was lowest being placed at the top, so that as far as possible a uniform layer of glue is produced on their surfaces. After air-drying, the strips are heated for 1 hour in the water-oven. Two or three lengths of 3 inches are cut out of the central portion of the strips. These are then separately tested by fixing between two indiarubber-covered clamps, one of which is fixed to the table and the other attached to the beam of a strong balance, the balance with the clamp, of course, being first counterpoised. Weights are added to the other pan until the paper breaks. A blank test is then made with the unsized paper, and this is deducted. Several experiments should be made, and the mean taken. A good glue should require some 9 or 10 lbs. when tested in this way to break the sized paper (*cf.* Gill, J. Ind. Eng. Chem. 1915, 7, 102; Rudeloff, Mitt. K. M. Materialproof, 1918, 36, 2; J. Soc. Chem. Ind. 1918, 37, 743, A).

Foam test. Trotman and Hackford (J. Soc. Chem. Ind. 1906, 104) recommend the following procedure: A graduated tube, 70 cm. in length and of such a diameter that each 1 cm. in length has a capacity of ·1 c.c., is half filled with a 10 p.c. solution of glue and placed in a water-bath. The temperature of the bath is maintained as nearly as possible at 60°. The tube is then corked, vigorously shaken for 1 min., and the top of the foam layer read off. The line of demarcation between the lower level of the foam and the liquid is too undefined to allow of reading, but that of the upper layer is constant. The peptones present in glue increase its tendency to foam.

The test is of importance for certain uses of glue, such as its application in veneering.

General remarks on the testing of glue.—Of course in each case, as already stated, the tests applied should refer directly to the uses to which the glue is to be put. For veneering and general joiner's work, for bookbinding and the like, a glue should have good tensile strength, little foaming power and good keeping qualities. It should also show a good jelly test and be free from grease, or it may give uneven joints. The glue for use in the sizing of canvas and the like should show a good strength of jelly and good tensile strength: foaming power and grease are of less importance. For the preparation of distempers, the grease content should be low, as it may give rise to 'flecks'; the keeping power should be high, but the tensile strength and strength of jelly are of less importance.

The specifications and tests of glue adopted by the American Society for Testing Materials, 1914, are as follows: Specifications for checking the quality of cabinet glue, should be based upon the viscosity, jelly-strength, odour, reaction, grease, foaming, ash, moisture, and appearance. The glue should be clean and free from an excessive number of air bubbles, the presence of the latter indicating decomposition during manufacture. About 6 p.c. of ash is the permissible maximum; the quantity usually found lies between 2·3 and 4·5 p.c. The glue should be neutral, or practically so to litmus paper. The jelly-strength is best ascertained by steeping the glue in cold water for 16 hours and then melting it at 160°F. (71°C.), the proportions of glue to water being such that the resulting jelly will contain from 7 to 10 p.c. of glue (7 p.c. in the case of higher-grade glues and 10 p.c. for lower qualities). The jelly is then cooled to about 45°F. (7°C.) and its firmness, judged by pressing with the fingers, is compared with that of a jelly prepared from a standard sample. Viscosity is determined at 30°C. in an Engler's viscometer, using a 15 p.c. glue solution; the time of flow for a high-grade glue is about 350 seconds. Glue should not contain any fatty substance, as determined by heating the glue solution with hydrochloric acid and extracting the cooled mixture with ether. Excessive foaming is undesirable; 300 c.c. of a 10 p.c. glue solution are heated for 1 minute to 150°F. (65°C.) in a beaker of about 2·5 inches diameter, when the layer of foam produced should not exceed 0·25 inch in depth (J. Soc. Chem. Ind. 1914, 33, 1021).

Hy. I.

GLUOTOL *v.* SYNTHETIC DRUGS.

GLUTAMIC ACID, *α-Aminoglutaric acid*

$CO_2H{\cdot}CH(NH_2)CH_2{\cdot}CH_2{\cdot}CO_2H$

was discovered by Ritthausen in 1866 (J. pr. Chem. [1] 99, 6, 454) among the products of the hydrolysis of wheat gluten by sulphuric acid, and hence called by him *glutaminic acid.* Subsequently, Ritthausen and Kreusler (J. pr. Chem. 1871, [2] 3, 214), Gorup-Besanez (Ber. 1877, 10, 780), Schulze (Zeitsch. physiol. Chem. 1892, 9, 253), and Wroblewski (Ber. 1898, 31, 3218) showed that it was formed by the hydrolysis of other vegetable proteids; and Hlasiwetz and Habermann (J. pr. Chem. 1873, [2] 7, 397), Panzer (Zeitsch. physiol. Chem. 1897, 24, 138), Abderhalden and Fuchs (*ibid.* 1908, 57, 339) isolated it from the products of hydrolysis of animal proteids. Abderhalden (*ibid.* 1913, 88, 478) found it in blood; Monti (Chem. Zentr. 1912, 1, 501) in tomato conserve; Kossel and Edlbacker (Zeitsch. physiol. Chem. 1915, 94, 264) in echinoderm; Meisenheimer in yeast (Chem. Zentr. 1915, ii. 1259). Osborne and Gilbert (Amer. J. Physiol. 1906, 15, 333) showed that the yield of glutamic acid from animal proteid matter varies from 7 to 10 p.c., whilst in vegetable proteids (with the exception of leucosine of wheat, 5·7 p.c.), the yield is larger, 12 to 37 p.c. A fruitful source of glutamic acid is beet-root molasses; Habermann (Annalen, 1875, 179, 248; Scheibler, Ber. 1884, 17, 1725; Andrlík, Zeitsch. Zuckerind. Böhm, 1903, 27, 665) obtained it to the extent of 7 p.c. on the dry solids of the molasses lye.

Kutscher (Zeitsch. physiol. Chem. 1899, 28, 123) isolated glutamic acid from the products of hydrolysis of casein by sulphuric acid, by precipitating the larger part of the organic bases with phosphotungstic acid, and removing the excess of sulphuric and phosphotungstic acids from the filtrate by means of barium hydroxide; the leucine and tyrosine crystallised out of the filtrate, and from the mother liquor the aspartic and glutamic acids were separated by the difference in solubility of their copper salts. Glutamic acid may be prepared from its hydrochloride by passing ammonia through the solution and evaporating to dryness; the greater part of the acid may be separated by fractional crystallisation, the remainder precipitated by alcohol (Abderhalden, Zeitsch. physiol. Chem. 1912, 77, 75).

For its isolation from molasses, *see* Stoltzenberg (Ber. 1913, 46, 557), who obtained the hydrochloride: Andrlík (Zeitsch. Zuckerind. Böhm, 1915, 39, 387), who obtained the acid from aqueous solution by means of tartaric sulphuric or phosphoric acid

Siegfried and Schmidt (Zeitsch. physiol. Chem. 1912, 81, 261) prepared the acid by means of the insoluble normal barium salt.

Ikeda and Suzuki (U.S. Pat. 1015891) separate glutamic acid from other hydrolysis products of albuminous substances by electrolysis; *see, also,* Scheermesser (Pharm. Zeit. 60, 487); Corti (J. Soc. Chem. Ind. 1917, 36, 979; Eng. Pat. 106081, 1916).

For the quantitative estimation of glutamic acid in the products of protein hydrolysis, *see* Foreman (Bio-Chem. J. 1914, 8, 465).

Glutamic acid contains an asymmetric carbon atom, and the dextro- and lævo-rotatory and the racemic variety of the acid are all known.

d-**Glutamic acid, the** naturally occurring compound, crystallises in the rhombic system $a:b:c=0{\cdot}6868:1:0{\cdot}8548$ (Oebbeke, Ber. 1884, 17, 1725); m.p. 208° (213° corr.) with decomposition (Fischer, Ber. 1889, 32, 2451); 224°–225° (corr.) decomposes (Abderhalden, Zeitsch. physiol. Chem. 1910, 64, 450); 211° when heated rapidly (Skola, Zeitsch. Zuckerind. Cechoslov. 1920, 44, 347), is sparingly soluble in water (the solubility is raised in presence of alkali and alkaline earth salts (Pfeiffer, Ber. 1915, 48, 1938), insoluble in alcohol or ether, and is practically insoluble in cold glacial acetic acid. It is dextro-rotatory in aqueous solution, $[\alpha]_D^{20°}+12{\cdot}04°$. According to Abderhalden and Kautzsch, $[\alpha]_D^{20°}=+31{\cdot}2°$

(Zeitsch. physiol. Chem. 1910, 64, 450). Fischer (Ber. 1899, 32, 2470) gives 30·85°. Increasing amounts of strong acid cause a continuous increase of the specific rotation, which tends towards a maximum. The addition of bases first changes the dextro- into lævo-rotation, which attains its highest numerical value with the formation of the acid salt, further quantities of base convert the lævo-rotation again into a dextro-rotation. With lead hydroxide, no change in sign of the rotation takes place (Andrlík, Zeitsch. verein, deut. Zuckerind, 1903, 572, 948; *see, also*, Pellet, Chem. Zentr. 1911, 1, 1766). Glutamic acid is converted into *l*-pyrrolidonecarboxylic acid to a large extent when its aqueous solution is boiled also to some extent at the temperature of the water-bath. After boiling a 2 p.c. aqueous solution for 100 hours, 90–95 p.c. of glutimic acid (pyrrolidone-2-carboxylic acid) is formed (Skola, Zeitsch. Zuckerind. Čechoslov. 1920, 44, 347). About 8 p.c. sulphuric acid and about 3 p.c. hydrochloric acid present in the solution inhibit the change; the *reverse* change occurs on boiling *l*-pyrrolidonecarboxylic acid with strong hydrochloric acid (Foreman, Bio-Chem. J. 1914, 8, 492); *see, also*, Fischer and Bœhner (Ber. 1911, 2, 1332). Staněk (Zeitsch. Zuckerind. Böhm, 1912, 371), on heating the aqueous solution above 200°, obtained *dl*-glutimic acid, below that temperature *l*-glutimic was the chief product.

A solution of *d*-glutamic acid (1 : 22,000) gives a characteristic colour reaction with triketohydrindene (Abderhalden and Schmidt, Zeitsch. physiol. Chem. 1913, 85, 143).

When glutamic acid is administered as a food, 96 p.c. is absorbed, a portion being used up in proteid synthesis, and the rest oxidised to urea (Andrlík and Velich, Zeitsch. Zuckerind. Böhm. 1908, 32, 313); its administration to phloridzinised dogs leads to increased elimination of dextrose in the urine (Warkalla, Beitr. Phys., 1914, 1, 91).

For its catabolism in the animal organism, *see* Ringer, Frankel (J. Biol. Chem. 1913, 14, 541). According to Roxas (J. Biol. Chem. 1916, 27, 77), it retards the action of tyrosinase on polypeptides.

Glutamic acid is decomposed by the action of bacteria, yielding *n*-butyric acid, together with small quantities of succinic and formic acids (Brasch and Neuberg, Biochem. Zeitsch. 1908, 13, 299, also under the action of certain microorganisms, yielding γ-aminobutyric acid (Ackermann, Zeitsch. physiol. Chem. 1910, 69, 273; Abderhalden, *ibid.* 1913, 85, 131). It breaks down under the action of sunlight to propaldehyde, ammonia, and carbon dioxide (Ganassini, Giorn. Farm. Chim. 1912, 81, 220). When oxidised by hydrogen peroxide, it yields succinic acid (Dakin, J. Biol. Chem. 1909, 5, 409); and yields γ-hydroxyglutaric acid (glutanic acid, *q.v.*), when treated with nitrous acid (Ritthausen, J. pr. Chem. [1] 103, 239). Natural *d*-glutamic acid is converted by nitrous acid into *l*-α-hydroxyglutaric acid, and by nitrosyl chloride or hydrochloric acid and nitrous acid into *l*-α-chloroglutaric acid, which in turn yields *d*-α-hydroxyglutaric (Fischer and Moreschi, Ber. 1912, 45, 2447).

For electrolytic diazotisation of the acid, *see* Krauss (J. Amer. Chem. Soc. 1917, 39, 1427).

d-Glutamic acid forms normal and acid salts, the latter being the more general. Of these, the *sodium* $C_5H_8O_4NNa$, *potassium* $C_5H_8O_4NK$, *calcium* $(C_5H_8O_4N)_2Ca$, *barium* $(C_5H_8O_4N)_2Ba$, *lead* $(C_5H_8O_4N)_2Pb$, are crystalline and hygroscopic. The calcium salt is converted to calcium pyrrolidone carboxylate on heating to 180°–185° (Abderhalden, Zeitsch. physiol. Chem. 1910, 64, 447); it is precipitated quantitatively from aqueous solution if sufficiently concentrated (Foreman, Bio-Chem. J. 1914, 8, 470). The normal barium salt is almost insoluble in water (Siegfried and Schmidt, Zeitsch. physiol. Chem. 1912, 81, 261). The glutamates of general formula $C_5H_8O_4NM'$ are largely soluble in water and have a characteristic taste. The manufacture and consumption of the sodium salt is general in Japan. Japanese seaweed, which is used for its flavour, has this taste (Ikeda, Orig. Com. 8th Intern. Cong. Appl. Chem. 18, 147). The normal *ammonium salt* $(NH_4)_2C_5H_7O_4N$ loses NH_3 at 110°–115°, and forms the *acid salt* $(NH_4)C_5H_8O_4N$; $[\alpha]_D$ about − 3·6° (Schulze and Trier, Ber. 1912, 45, 257). The blue copper derivative

$$(C_5H_9O_4N)_5, 4\,CuO, 7\tfrac{1}{2}H_2O$$

is crystalline; *zinc*, and *cadmium* salts, and *cobalt* and *nickel* derivatives have been prepared (Hugounenq and Florence, Bull. Soc. Chim. 1920 [iv], 27, 750). The *copper salt* $C_5H_7O_4NCu,\frac{1}{2}H_2O$ is amorphous and greenish-blue, and dissolves in 400 parts boiling water (Wolff, Annalen, 1890, 260, 79); the *silver salts* $C_5H_7O_4NAg_2$ and $C_5H_8O_4NAg$ are white insoluble powders; the *ferrous salt* is obtained when glutamic acid is boiled with an excess of iron powder in an oxygen-free atmosphere (Hoffmann, D. R. P. 264390); the *zinc salt* is basic $(C_5H_8O_4N)_2Zn,ZnO$; the *mercuric salt* a heavy crystalline powder decomposing 208°–209° (Habermann, Annalen, 1871, 179, 248; Abderhalden and Kautzsch, Zeitsch. physiol. Chem. 1910, 64, 447; 68, 487; and *ibid.* 1912, 78, 333). The *hydrochloride* has m.p. 202° (decomp.), or, heated quickly, m.p. 210° (Abderhalden, Zeitsch. physiol. Chem. 1910, 64, 450); $[\alpha]_D^{20°}+25°$ (*ibid.*); or 24·5° (Fischer and Bœhner, Ber. 1911, 44, 1334). For crystallography of hydrochloride, *see* Kaplanova (Abh. Bhöm. Akad. 1915, No. 23, 8 pp.; from Jahrb. Min. 1917, 1, 123). The *strychnine* salt has m.p. 225°–230° $[\alpha]_D^{20°}-25·5°$; the *brucine* salt has m.p. 240° $[\alpha]_D^{20°}-23°$ (Dakin, Biochem. J. 1919, 13, 398). For the *imido-orthophosphoric ester* $C_7H_{14}O_7NP$ of glutamic acid, *see* Langheld (Ber. 1911, 44, 2076). *dl-Glutamic-picrolonate* crystallises in fine short spindles which decompose 184°, *d*-glutamic picrolonate has $[\alpha]_D^{20°}+85°$ (Levene and van Slyke, J. Biol. Chem. 1912, 12, 127). The *ethyl ester* $C_5H_8(C_2H_5)O_4N$ is crystalline, and melts at 188° (Menozzi and Appiani, Gazz. chim. ital. 1894, 24, i. 384); the *diethyl ester* has b.p. 139°–140°/10 mm., sp.gr. 1·0737 at 17°, and $[\alpha]_D^{20°}+7·34$ (Fischer, Sitzungsber. Akad. Wiss. Berlin, 1900, 48, 1062).

Glutamic acid forms a soluble benzene sulphonyl derivative, $SO_2Ph{\cdot}NH(C_3H_5)(CO_2H)_2$ (Hedin, Ber. 1890, 23, 3196); and the following *acyl* derivatives are described by Fischer (Ber. 1907, 40, 3704), Fischer, Kropp and Stahlschmidt (Annalen, 1909, 365, 181): *l-leucyl-d-glutamic acid*

$$CHMe_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO{\cdot}NH{\cdot}CH(CO_2H){\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H,$$

m.p. 232° (decomp. corr.), has $[\alpha]_D^{20°}+10{\cdot}5°$ in N/1-HCl, forms soluble sodium and barium salts, the silver salt being sparingly soluble; *chloracetyl-d-glutamic acid*

$$CH_2Cl{\cdot}CO{\cdot}NH{\cdot}CH(CO_2H){\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H,$$

m.p. 143° (corr.), $[\alpha]_D^{20°}-13{\cdot}5°$ (±0·2°) in aqueous solution, yields *glycyl-d-glutamic acid*

$$NH_2{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CH(CO_2H)[CH_2]_2CO_2H,$$

m.p. 178° (corr.), $[\alpha]_D^{20°}-6{\cdot}3°$; *chloracetylglutamyldiglycinediethyl ester*

$$CH_2Cl{\cdot}CO{\cdot}NH{\cdot}CH\begin{cases}CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2Et\\CH_2{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2Et\end{cases}$$

m.p. 146° (corr.), yields on hydrolysis *chloracetylglutamyldiglycine* $C_{11}H_{16}O_7N_3Cl$, m.p. 173° (decomp. corr.), and yields on treatment with aqueous ammonia *glycylglutamyldiglycine* $C_{11}H_{18}O_7N_4$, m.p. 248° (corr.). *Phenylacetylglutamic acid* $C_{13}H_{15}O_5N$, microscopic needles, has m.p. 123°, $[\alpha]_D$ −19° in 3–10 p.c. aqueous solution; the brucine salt

$$C_{13}H_{15}O_5N{\cdot}2C_{23}H_{26}O_4N_2$$

has $[\alpha]_D$ −1·37° (Thierfelder, Sherwin, Zeitsch. physiol. Chem. 1915, 94, 1; Ber. 1915, 47, 2630).

r-**Glutamic acid** has been synthesised by Wolff (Annalen, 1890, 260, 79) from lævulic acid. Glyoxylpropionic acid

$$OHC{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$$

obtained by boiling dibromolævulic acid with water, reacts with hydroxylamine to form γδ-di*iso*nitrosovaleric acid

$$CH(NOH)C(NOH)CH_2{\cdot}CH_2{\cdot}CO_2H,$$

from which *iso*nitrosocyanobutyric acid

$$CN{\cdot}C(NOH){\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$$

is obtained by hydrolysis with sulphuric acid and subsequent treatment with cold sodium hydroxide. When *iso*nitrosocyanobutyric acid is hydrolysed with boiling alkali, it yields *iso*nitrosoglutaric acid

$$CO_2H{\cdot}C(NOH){\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H,$$

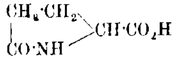
and this is reduced to inactive glutamic acid

$$CO_2H{\cdot}CH(NH_2)CH_2{\cdot}CH_2{\cdot}CO_2H$$

by tin and hydrochloric acid. *r*-Glutamic acid can be prepared from the dextro- isomeride by heating it with barium hydroxide (Schulze and Bosshard, Ber. 1885, 18, 388; Schulze, Zeitsch. physiol. Chem. 1892, 9, 253).

r-Glutamic acid crystallises from hot water in rhombic plates, *a* : *b* : *c*=0·7454 : 1 : 1·2367, m.p. 199° (decomp. corr.), dissolves in 66·7 parts water at 20°, and is sparingly soluble in ether, alcohol, carbon disulphide, or light petroleum. The *copper salt* $C_5H_7O_4NCu,2\frac{1}{2}H_2O$ forms blue needles, becomes anhydrous at 135°, and is not soluble in less than 1000 parts of boiling water. The *hydrochloride* crystallises in needles, m.p. 193° (decomp.) (Wolff), 200° (Abderhalden and Kautzsch, Zeitsch. physiol. Chem. 1910, 68, 487), and is crystallographically identical with the hydrochloride of the *d*-acid, *a* : *b* : *c*=0·8873 : 1 : 0·3865 (Wolff, *l.c.*).

When *r*-glutamic acid is heated at its melting-point, it decomposes, yielding *pyrrolidonecarboxylic acid*



This compound has m.p. 182°–183°, and is identical with the pyroglutamic acid obtained by Haitinger (Monatsh. 3, 228) by heating *d*-glutamic acid, and also with the glutimic acid of Schutzenberger (Ann. Chim. [5] 16, 372), obtained by decomposing albumin with barium hydroxide at 180° (compare also Abderhalden and Kautzsch, Zeitsch. physiol. Chem. 1910, 68, 487). *r-Benzolyglutamic acid* crystallises with $1H_2O$, m.p. 152°–153° (155°–157° corr.), and is soluble in 124 parts of water at 20° (Fischer, Ber. 1899, 32, 2451). *Chloracetyl-r-glutamic acid* has m.p. 123°; *glycyl-r-glutamic acid* is a hygroscopic powder, and forms a *copper salt* crystallising with $3\frac{1}{2}H_2O$ that decomposes at 223° (corr.) (Fischer, Kropp and Stahlschmidt, Annalen, 1909, 365, 181).

l-**Glutamic acid.** When *r*-glutamic acid is crystallised from water, right- and left-handed enantiomorphous crystals are deposited, but this fact cannot conveniently be utilised for the preparation of the *l*-isomeride; this was, however, effected by the cultivation of *Penicillium glaucum* in a solution of the *r*-acid, whereby the *d*-acid is destroyed and the *l*-acid remains in solution (Menozzi and Appiani, Gazz. chim. ital. 1894, 24, i. 370). Fischer (Ber. 1899, 32, 2451) resolved *r*-benzoylglutamic acid by the fractional crystallisation of the strychnine salt; *benzoyl-l-glutamic acid* has m.p. 130°–132° (corr.), dissolves in less than two parts of water at 100°, or 21 parts at 20°, and has $[\alpha]_D+13{\cdot}81°$ in 5 p.c. aqueous solution, and the potassium salt has $[\alpha]_D-18{\cdot}7°$: it yields *l-glutamic acid* on hydrolysis, and this is identical with the *d*-isomeride, except that it has $[\alpha]_D^{20°}-30{\cdot}05°$, whilst the *d*-acid has +30·45°.

l-Pyrrolidonecarboxylic acid, obtained by heating *d*-glutamic acid at 150°–160°, forms large colourless orthorhombic crystals, m.p. 162°, *a* : *b* : *c* =1·5034 : 1 : 1·6292, and has $[\alpha]_D$ −11·5° (Menozzi and Appiani, Gazz. chim. ital. 1894, 24, i. 370; Abderhalden and Kautzsch, Zeitsch. physiol. Chem. 1910, 68, 487). For the conversion of glutamic acid or pyrrolidonecarboxylic acid into proline, *see* Fischer and Boehner (Ber. 1911, 44, 1332).

β-Hydroxyglutamic acid

$$CO_2H{\cdot}CH(NH_2)CH(OH){\cdot}CH_2{\cdot}CO_2H$$

has been isolated from the products of acid hydrolysis of caseinogen; it crystallises in stout prisms, has $[\alpha]_D^{20°}$ about +0·8° in 4 p.c. aqueous solution, and $[\alpha]_D^{20°}+16{\cdot}3°$ in 2 p.c. hydrochloric acid solution. On prolonged heating at 100°–110° over phosphorous pentoxide it yields hydroxypyrrolidonecarboxylic acid. It yields *silver, copper, mercury, lead, cadmium, zinc, calcium*, and *barium salts*, and gives a diethyl ester. The *strychnine* salt has m.p. 245°, $[\alpha]_D^{20°} -26·3°$. The *brucine* salt has $[\alpha]_D^{20°} -25·0°$ and decomposes at about 200°. The synthesis of the compound from glutamic acid has been effected (Dakin, Biochem. J. 1918, 12, 290; 1919, 13, 398). M. A. W.

GLUTAMINE $CO_2H·C_3H_6(NH_2)CONH_2$ is the half amide of glutamic acid. It was discovered in 1877 by Schulze and Urich (Ber. 10, 85) in the juice of young pumpkin plants, and isolated from beet root sap by Schulze and Bosshard (*ibid.* 1883, 16, 312), one litre yielding 0·7 to 0·9 gram of glutamine; *see, also,* Smolenski (Chem. Zentr. 1911, 1, 518, from Zeitsch. Ver. Dtsch. Zuckerind. 1910, 1215). It appears to replace its homologue asparagine in some natural orders, *e.g.* *Caryophyllaceæ*, *Cruciferæ*, and *Filices*, where it occurs in the leaves, seedlings, roots, and tubers. The greatest amount of glutamine found in seedlings is only 2·5 p.c. of the dry matter which is much less than the amount of asparagine found in leguminous seedlings, but it is probable that, owing to the difficulties of separating glutamine, the plant contains at least twice as much as is actually isolated (Schulze, Zeitsch. physiol. Chem. 1894, 20, 327; 1897, 24, 18; Ber. 1896, 29, 1882; Landw. Versuchs.-Stat. 1898, 49, 442: Deleano, Zeitsch. physiol. Chem. 1912, 80, 79). Glutamine occurs with asparagine in the juice of ripening oranges (Scurti and De Plato, Chem. Zentr. 1908, ii. 16, 1370): for distribution in plants, *see, also,* Stieger (Zeitsch. physiol. Chem. 1913, 86, 245) According to Thierfelder and von Cramm, glutamine is a component of the protein molecule (Zeitsch physiol. Chem. 1919, 105, 58).

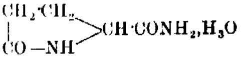
Glutamine crystallises in needles; it dissolves in about 25·7 parts of water at 16° (Schulze and Godet, Landw. Versuchs.-Stat. 1907, 67, 313), and is sparingly soluble in alcohol. It behaves as a very weak acid towards indicators (Sellier, Chem. Zentr. 1904, i. 789). Glutamine is dextro-rotatory in aqueous solution, seven specimens from various vegetable sources were found to have $[\alpha]_D$ between +1·9° and +9·5°, the differences being probably due to the presence of the two stereoisomerides in varying proportions (Schulze and Bosshard, Ber. 1885, 18, 390; Sellier, Chem. Zentr. 1904, i. 789; Schulze, Ber. 1906, 39, 2932; Landw. Versuchs.-Stat. 1906, 65, 237). Schulze and Trier (Ber. 1912, 45, 257) found that a 4 p.c. aqueous solution of glutamine, obtained from its purified copper salt, has $[\alpha]_D^{20°} +6°$ to +7°; a 7–8 p.c. acid solution (5 p.c. hydrochloric acid) has $[\alpha]_D^{20°} +31°$ to +32°; compare Pellet (Chem. Zentr. 1911, 1, 1766, from Zeitsch. Zuckerind. Böhm, 35, 437), who recommends estimating the rotation in hydrochloric acid solution.

The estimation of glutamine is best effected by Schlösing's method (Schulze, J. pr. Chem. 1885, [2] 31, 233), as the $-CO·NH_2$ group is completely hydrolysed when distilled with magnesia under the ordinary pressure, but if the pressure be reduced sufficiently to cause the solution to boil at 40°, hydrolysis does not take place, and under these conditions ammonium salts may be completely removed (Sellier, Bull. Soc. chim. Sucr. Dist. 1907, 25, 124; Schulze, Landw. Versuchs.-Stat. 1906, 65, 237). For the catabolism of glutamine in the organism, *see* Thierfelder and Sherwin (Zeitsch. physiol. Chem. 1915, 94, 1); also Sherwin, Wolf and Wolf (J. Biol. Chem. 1919, 37, 113).

Owing to the feebly acidic character of glutamine, very few salts have been isolated: the *copper* derivative, $Cu(C_5H_9O_3N_2)_2$, forms bluish violet crystals, the *cadmium* derivative, $Cd(C_5H_9O_3N_2)_2$, forms fine prisms; and is decomposed by boiling water. Glutamine forms a *compound* with tartaric acid, that separates in large transparent crystals (Schulze and Godet, Landw. Versuchs.-Stat. 1907, 67, 313). Phenylacetylglutamine has $[\alpha]_D -18°$ in 2–4 p.c. aqueous solution; the specific rotation decreases in hydrochloric acid solution (Thierfelder and Sherwin, *l.c.*). For a description of dipeptides and tripeptides containing glutamine, see Thierfelder and von Cramm (Zeitsch. physiol. Chem. 1919, 105, 58); also Abderhalden and Spinner (Zeitsch. physiol. Chem. 1919, 107, 1).

By the action of alcoholic ammonia on the ester of *d*- or *l*-glutamic acid, the amide of the corresponding pyrrolidonecarboxylic acid is formed; these are called *glutimides* by Menozzi and Appiani, and the dextro- and lævo-rotatory and the racemic variety are described.

d-**Glutimide**

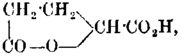


$$\begin{matrix} CH_2·CH_2 \\ | \\ CO-NH \end{matrix} \!\!>\! CH·CONH_2,H_3O$$

crystallises in needles belonging to the anorthic system, $a:b:c = 1·403:1:1·421$, $\beta = 86·55°$; it has m.p. 165°, and $[\alpha]_D +41·29°$. *l-Glutimide* has $[\alpha]_D -40°$, and has the same melting-point and other properties as its dextro-isomeride. *r*-Glutimide is formed when *l*-glutimide is heated with alcoholic ammonia at 140°–150°, or alone at 200°; it has m.p. 214°, and crystallises in the orthorhombic system, $a:b:c = 0·8853:1$ 0·3866 (Menozzi and Appiani, Atti. R. Accad. Linc. 7, i. 33; Gazz. chim. ital. 1894, 24, i. 370).

M. A. W.

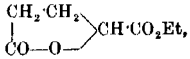
GLUTANIC ACID, *a-hydroxyglutaric acid*, is formed when nitrous acid reacts with glutamic acid (Markownikoff, Annalen, 1876, 182, 347); it occurs in molasses, and was isolated in the form of the zinc salt from the ethereal extract of the product of the action of dilute nitric acid at 70° on casein (Habermann and Ehrenfeld, Zeitsch. physiol. Chem. 1902, 35, 231). The *zinc salt* $C_5H_6O_5Zn,3H_2O$ and the *magnesium salt* $C_5H_6O_5Mg,4H_2O$ are well defined (Markownikoff, *l.c.*). The free acid has not been isolated, but forms *butyrolactone-γ-carboxylic acid*



$$\begin{matrix} CH_2·CH_2 \\ | \\ CO-O- \end{matrix} \!\!>\! CH·CO_2H$$

, m.p. 49°–50°, when an aqueous solution is evaporated at 100°, and the resulting syrup allowed to crystallise over sulphuric acid.

Ethylbutyrolactonecarboxylate



$$\begin{matrix} CH_2·CH_2 \\ | \\ CO-O- \end{matrix} \!\!>\! CH·CO_2Et,$$

prepared by the action of epichlorhydrin on ethylsodiomalonate, is a colourless oil, b.p. 175°/25 mm. (Traube and Lehmann, Ber. 1901, 34, 1971).

Natural *d*-glutamic acid is converted by nitrous acid into *l*-α-hydroxyglutaric acid, which has a very small lævo-rotation. The *sodium* salt has $[\alpha]_D^{19°} - 8{\cdot}65°$ Nitrosyl chloride transforms *l*-α-hydroxyglutaric acid into *l*-α-chloroglutaric acid, m.p. 99° (corr.), $[\alpha]_D^{18°} - 12{\cdot}5°$, and this yields *d* α-hydroxyglutaric acid $[\alpha]_D^{25°} + 8{\cdot}58°$. (Fischer and Moreschi, Ber. 1912, 45, 2447). The Walden inversion in the case of α-hydroxyglutaric acid and its derivatives, has been examined by Karrer and Kaase (Helv. Chim. Acta, 1919, 2, 436). M. A. W.

GLUTARIC ACID $C_5H_8O_4$. Glutaric acid and its alkyl derivatives, when heated, break down into anhydrides and water. The anhydrides readily yield anilic acids, from which anils can be obtained by the withdrawal of water (Auwers, Oswald, and Thorpe, Annalen, 285, 229). The glutaric acids resemble the succinic acids in their reactions, but they are not so volatile in steam, and not so readily changed to anhydrides by acetylchloride.

Glutaric acid. Normal Pyrotartaric acid.

$CO_2H[CH_2]_3CO_2H$

Found in Caucasian naphtha (Markownikow, Ber. 1897, 947), in beet-root (Lippmann, *ibid.* 1891, 3299), and in the wash-water from raw sheep wool. Prepared by oxidising fats (Bouveault, Bull. Soc. chim. 19, [3] 562), stearic and oleic acids (Carette, *ibid.* 46, 65) or sebacic acid (Carette, *ibid.* 45, 270), with nitric acid; by treating 1 : 3-dicyanopropane with hydrochloric acid (Reboul, Ann. Chim. 14, [5] 14, 501; Markownikow, Annalen, 182, 341); by treating β-hydroxyglutaric acid with hydriodic acid at 180° (Pechmann and Jenisch, Ber. 1891, 3252); by the action of baryta on ethyl pentanehexacarboxylate (Bottomley and Perkin, Chem. Soc. Trans. 1900, 300); by treating ethyl malonate with methylene chloride, hydrolysing the product with caustic potash and heating the dicarboxylglutaric acid thus formed to 200° (Conrad and Guthzeit, Annalen, 222, 257; Perkin, Ber. 1886, 1055); by condensing ethylsodiomalonate with formaldehyde in the presence of a small quantity of piperidine or diethylamine, and heating the methylene dimalonic acid thus formed with hydrochloric acid (Knoevenagel, Ber. 1894, 2346); by the electrolysis of equal quantities of the potassium salts of the methyl hydrogen succinate and malonate (Vanzetti and Coppadro, Chem. Zentr. 1904, i. 1254; 1903, ii. 1053); by treating hydroresorcin with sodium hypobromite (Vorlander and Kohlmann, Ber. 1899, 1878); by treating cyclopentanone with nitric acid (Wislicenus, Annalen, 275, 318) or with acetic anhydride, and subsequently with potassium permanganate (Mannich and Hancu, Ber. 1908, 572); by the action of nitric acid on methylcyclopentane (Markownikow, *ibid.* 1900, 1908), or on cyclopentane (Markownikow, *ibid.* 1897, 975); by treating α-acetoglutaric ester with concentrated potash (Vorlander and Knötzsch, Annalen, 294, 315; Wislicenus and Limpach, *ibid.* 192, 128); by treating glutaconic acid with sodium amalgam (Conrad and Guthzeit, *ibid.* 222, 254); by the oxidation of piperidine with hydrogen peroxide (Wolffenstein, Ber. 1892, 2777).

Glutaric acid crystallises in large monoclinic plates, m.p. 97·5°; 100 c.c. of water dissolve 42·9 parts of acid at 0°, 63·9 at 20°, and 95·7 at 50° (Lamouroux, Compt. rend. 128, 998); readily soluble in alcohol and ether. It condenses with aldehydes to form substituted glutaric acids (Fittig and Roedel, Annalen, 282, 334, 338, 344; Knoevenagel, Ber. 1894, 2346); electrolysis of the potassium salt of the monoethyl ester gives rise to the diethyl ester of suberic acid (Brown and Walker, Annalen, 261, 119). By heating glutaric acid at 230°–280°, or by treating the silver salt with acetyl chloride, *glutaric anhydride*, m.p. 56°–57°, is produced (Fichter and Herbrand, Ber. 1896, 1193). When treated with aluminium amalgam, the anhydride is converted into a mixture of glutaric and δ-hydroxyvaleric acids, the latter of which readily changes into δ-hydroxyvalerolactone (Fichter and Beisswenger, Ber. 1903, 1200)

The *dimethyl ester of glutaric acid* is a colourless liquid, b.p. 213·5°–214° (751 mm.), sp.gr. 1·09337 15°/4° (Meerburg, Rec. trav. chim. 1899, 367); the *diethyl ester* boils at 236·5°–237° (corr.), and has sp.gr. 1·0284 at 15° (Perkin, Chem. Soc. Trans. 1888, 567).

The three possible isomerides of glutaric acid are all known and are described below.

Pyrotartaric acid. Methylsuccinic acid (Ger. *Brenzweinsaüre*; *Methylbernsteinsaüre*)

$CO_2H{\cdot}CH(CH_3){\cdot}CH_2{\cdot}CO_2H$

Obtained from suint (Buisine, Compt. rend. 107, 789). Prepared by the dry distillation of tartaric, racemic, or pyruvic acids (Fourcroy and Vauquelin, Ann. Chim. 35, (i.) 161; 64, 42; Wolff, Annalen, 317, 22; Béchamp, Zeitsch. Chem. 1870, 371; Bourgoin, Ann. Chim. 12, [5] 419); by heating pyruvic acid with hydrochloric acid (Wolff, *l.c.*; Jong, Rec. trav. chim. 21, 191); by the reduction of citra-, ita-, or mesaconic acids with sodium amalgam (Kekulé, Annalen, Spl. 1, 338; Spl. 2, 95); by the reduction of the anhydride of citraconic acid with hydrogen in the presence of nickel, when pyrotartaric acid and its anhydride are produced (Eijkman, Chem. Zentr. 1907, i. 1617); by treating β-cyanobutyric acid with caustic potash (Wislicenus, Annalen, 165, 93; Bredt and Kallen, *ibid.* 293, 350); by fusing gamboge with caustic alkali (Hlasiwetz and Barth, *ibid.* 138, 73); by treating aldehydo*iso*butyric acid with nitric acid (Perkin and Sprankling, Chem. Soc. Trans. 1899, 19; Bischoff and Kuhlberg, Ber. 1890, 634); by the interaction of ethylsodiomalonate with ethylbrompropionate and subsequent boiling with hydrochloric acid (Bone and Sprankling, Chem. Soc. Trans. 1899, 848); by the interaction of ethylsodiomethylmalonate and ethylchloracetate or of ethylsodioethenyltricarboxylate and methyliodide, and subsequently hydrolysing the ester of methylethenyltricarboxylic acid thus formed (Bischoff and Kuhlberg, *l.c.*); by treating ethyldibromomethylacetoacetate with concentrated potash and subsequently with sulphuric acid (Cloez, Compt. rend. 110, 583); by treating calcium lactate with potassium permanganate, when calcium pyrotartrate is produced (Wiegand, Ber. 1884, 840).

Pyrotartaric acid crystallises in triclinic prisms, m.p. 117°–118° (Ladenburg), 112° (Perkin). Soluble in water, alcohol, and ether.

By heating pyrotartaric acid with dilute sulphuric acid at 150°, acetaldehyde and formic acid are produced (Wiegand, *l.c.*); by condensation with acetaldehyde, benzaldehyde, &c., substituted paraconic acids are produced (Fittig, Annalen, 255 ; 108, 126, 257); with salicaldehyde coumarinpropionic acid is produced (Fittig and Brown, *ibid.* 255, 285). Methylthiophen is produced by the distillation of the sodium salt with phosphorus pentasulphide. Pyrotartaric acid contains an asymmetric carbon atom, and it has been resolved into its two optically active antipodes by means of the fractional crystallisation of its strychnine salt (Ladenburg, Ber. 1895, 1170 ; 1896, 1254 ; Annalen, 364, 227).

Pyrotartaric anhydride is obtained by heating the acid above 200°, or by treating the acid with acetylchloride (Perkin, Chem. Soc. Trans. 1888, 564 ; Fichter and Herbrand, Ber. 1896, 1193) ; m.p. 31·5°–32° ; b.p. 247·4° (corr.), sp.gr. 15°/15°, 1·2378. By reduction with hydrogen in the presence of nickel, the anhydride yields butyrolactone (Eijkman, Chem. Zentr. 1907, i. 1617), and with sodium amalgam and hydrochloric acid, *a*-methylbutyrolactone (Fichter and Herbrand, *l.c.*).

The *dimethyl ester* of *pyrotartaric acid* is a colourless oil, b.p. 197° ; and the *diethyl ester* boils at 217·5–218·5°.

Dimethylmalonic acid, β-Isopyrotartaric acid $(CH_3)_2C(CO_2H)_2$. Obtained by the oxidation of fenchone with nitric acid (Gardner and Cockburn, Chem. Soc. Trans. 1898, 708) ; by the oxidation of phoronic acid with nitric acid or with potassium permanganate in alkaline solution (Pinner, Ber. 1882, 585 ; Anschütz, *ibid.* 1893, 827 ; Anschutz and Walter, Annalen, 368, 95) ; by the oxidation of filicinic acid, obtained from filicin, which is extracted from *Filix mas* (male fern) (Boehm, Chem. Zentr. 1896, ii. 1036 ; Daccomo, Gazz. chim. ital. 24, 1, 517) ; by the oxidation of camphor with nitric acid (Bredt, Ber. 1894, 2093). Prepared by treating *a*-cyan*iso*butyric acid with hydrochloric acid (Markownikow, Annalen, 182, 336) ; by heating 5 : 5-dimethylbarbituric acid with caustic potash (Conrad and Guthzeit, Ber. 1881, 1644) ; by the oxidation of *aa*-dimethylglutaconic acid with potassium permanganate (Henrich, Ber. 1899, 670 ; Perkin, Chem. Soc. Trans. 1902, 255).

Dimethylmalonic acid is best obtained pure from its zinc salt ; m.p. 190° (Perkin, Chem. Soc. Trans. 1903, 1237), 192°–193° (Königs and Hörlin, Ber. 1893, 2049) ; sparingly soluble in water and alcohol, readily soluble in ether ; decomposes on heating into carbon dioxide and *iso*butyric acid. Dimethylmalonylchloride yields a duodecimolecular anhydride on treatment with aqueous pyridine ; it is an amorphous white powder, m.p. 145°–148° (Einhorn, Annalen, 359, 169). *Dimethylmalononitrile* is prepared by treating dimethylcyanacetamide with phosphoric oxide or phosphorus pentachloride (Hesse, Annalen, 18, 723 ; Errera and Berti, Gazz. chim. ital. 26, ii. 224), m.p. 32°, b.p. 162·5°. *Dimethylmalonamide* is prepared from the methyl ester and concentrated aqueous ammonia (Perkin, Chem. Soc. Trans. 1903, 1242 ; Thorne, *ibid.* 1881, 545) ; from the ethyl ester and alcoholic ammonia (Fischer and Dilthey, Ber. 1902, 851, 855) ; from dimethylmalonylchloride and concentrated aqueous ammonia (Meyer, Ber. 1906, 198), m.p. 269° (corr.) (Perkin). The *dimethyl ester* is a colourless liquid, b.p. 177°–178° (753 mm.) ; the *diethyl ester* boils at 194·5°. The latter may be obtained by treating the ester of dimethylcyanacetic acid with sulphuric acid : on treatment with alkali and urea, dimethylbarbituric acid is obtained (Merck, Chem. Zentr. 1905, ii. 1141 ; D. R. P. 163200). The diethyl ester of dimethylmalonic acid condenses with brom*iso*butyric ester in the presence of zinc to form the ester of tetramethylacetonedicarboxylic acid (Shdanowitsch, Chem. Zentr. 1907, i. 519). The potassium salt of the monoethyl ester is converted by electrolysis into the diethyl ester of tetramethylsuccinic acid (Brown and Walker, Annalen, 274, 48).

Ethylmalonic acid. Isopyrotartaric acid

$$CH_3{\cdot}CH_2{\cdot}CH(CO_2H)_2$$

Prepared by boiling the ethyl ester of *a*-cyanobutyric acid with potash (Wislicenus and Urech, Annalen, 165, 93 ; Tuoplew, *ibid.* 171, 243 ; Markownikow, *ibid.* 182, 329) ; the diethyl ester is produced by treating ethyl malonate with sodium or zinc and ethyl iodide (Daimler, *ibid.* 249, 174 ; Schukowsky, Chem. Soc. Abstr. 1888, 1179 ; Schey, Rec. trav. chim. 16, 356 ; Michael, J. pr. Chem. 72, [2] 537). Crystallises in rhombic prisms, m.p. 111·5° ; readily soluble in water, alcohol, and ether ; decomposes on heating into butyric acid and carbon dioxide.

Ethylmalononitrile is prepared from ethylcyanacetamide and phosphorus pentachloride ; it is a colourless oil, b.p. 200° (Hessler, Annalen, 1899, 169 ; Henry, J. 1889, 637). *Ethylmalonamide* is prepared by the action of sodium ethoxide and ethyl iodide on malonamide (Meyer, Monatsh. 28, 1 ; Conrad and Schulze, Ber. 1909, 730) ; by treating the diethyl ester with concentrated aqueous ammonia (Freund and Goldsmith, *ibid.* 1888, 1245) ; m.p. 214°. The *diethyl ester* boils at 207° ; when the sodium derivative of this ester is condensed with ethylbrommalonate in alcoholic solution, the ethyl ester of ethylenetetracarboxylic acid is produced (Bischoff, Ber. 1896, 1514).

GLUTEN. Wheaten flour differs from that of all other cereals in that after it has been made into a dough with a little water, it is possible to wash out the starch, leaving a sticky adhesive brown or greyish-brown residue which consists mainly of protein. This is crude gluten : on drying it in a water-oven, a hard, brittle horny mass, not unlike glue, results, which has lost its power of becoming plastic when wetted, and strongly adheres to the substance on which it rests. At a higher temperature, the wet gluten expands greatly until the expansive force ruptures its vesicles.

The flour of other cereals when washed in a similar way entirely disintegrates, leaving no protein residue. The physical properties of wheaten dough depend almost entirely on the gluten, which acts as a mechanical agency for binding the particles of starch and for entangling the carbon dioxide gas produced by the fermentation : in the oven, this gas expands, causing the dough to rise and the gluten to remain distended until the heat fixes it.

Crude gluten varies in colour from grey to brown. Besides protein, it contains traces of starch, fibre, cholesterol, fat, and a small proportion of mineral matter. It is insoluble in tap water, strong alcohol, and ether, but dissolves partly in distilled water, in dilute alkalis and more slowly in dilute acids.

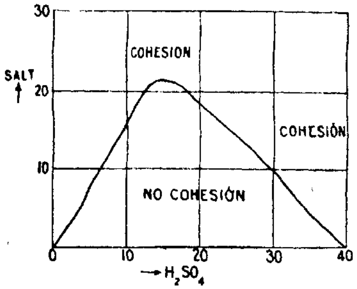
Gluten, after treatment with dilute acids or salts, has some diastatic action, which the freshly prepared gluten lacks (Reychler, Ber. 1889, 22, 414; *see also* Baker, J. Soc. Chem. Ind. 1908, 27).

The quantity of gluten in wheaten flour varies considerably according to its race and the country in which it was grown. Further, the best patent flour, milled from the centre of the grain, contains slightly less gluten than the households flour from the outer layers of the same grain.

Speaking very generally, the proportion of gluten varies from 8 to 15 p.c., though exceptional flours may have either less or more than this amount. English flours as a class have about 10 p.c. or less gluten, Canadian and American spring wheat flours, *e.g.* the so-called No. 1 Manitoba, contain 13 p.c. and upwards. The strength of a flour depends, however, not so much on the quantity of gluten present as on its quality. A gluten, though present in satisfactory quantity, may be too tough, or hard and brittle, or it may be too elastic and have no power of retaining the gas in its pores.

Gluten consists mainly of two proteins, *gliadin* and *glutenin*, both of which are essential for its formation. The gliadin forms a sticky network which entangles the glutenin to make a compact mass. The presence of soluble salts, *i.e.* electrolytes, is also essential, but the mineral constituents of the flour are sufficient for this purpose. In distilled water, gluten partly dissolves, the semi-fluid residue having no tenacity. Pure gluten has of itself neither ductility nor tenacity, and the physical properties like those of other colloidal substances depend upon the electrolytes present in the dough.

The researches of Wood and Hardy (Wood, J. Agric. Sci. 1907, 2, 139, 267; Wood and Hardy, Proc. Roy. Soc. 1909, B, 81, 38; Summary by Hardy, Brit. Assoc. Report, Winnipeg, 1909) have shown that any salt confers cohesion upon gluten; any acid or alkali, when sufficiently dilute, lessens or destroys it. Gluten which has lost cohesion owing to the action of an acid, may be rendered coherent again by the addition of salt. There is a definite relation between the concentration of the acid and the amount of salt required to undo its action. As the concentration of the acid is increased, the amount of salt needed to maintain cohesion rises to a maximum, and thence falls until a point is reached when the acid alone is sufficient. The curve shows the concentration of salt and acid needed just to preserve cohesion: it encloses an area of no cohesion, whilst outside it is a region of cohesion. The areas represent continuous changes as is characteristic of colloidal matter: a line inclined upwards follows a system in which there is continual separation of water and gluten; in consequence the water-holding power of the protein becomes less and less, the tenacity grows, and the ductility diminishes.



Upson and Calvin (J. Amer. Chem. Soc. 1915, 37, 1295-1304) have shown that moist gluten absorbs water from acid solutions in quantity varying with the nature and concentration of the acid. The presence of neutral salts retards the absorption of water, and in high concentrations may even cause a loss of water from moist gluten. If gluten which has absorbed water in an acid solution be transferred to a salt solution it loses water and regains its original physical properties. Non-electrolytes are much less effective than electrolytes in inhibiting the swelling of gluten in acid solutions.

In practice, the water-holding capacity, or *hydration ratio*, of gluten is of considerable significance. It is measured by the ratio of the weight of the wet gluten immediately after extraction under carefully standardised conditions to its weight after drying. On the average, it is about 3 : 1; that is, gluten carries about twice its weight of water. It varies from 2·5 in strong flours to above 3 in very weak flours.

The ratio of gliadin to glutenin in different wheats is not constant. It appears to be about 50 p.c. According to Shutt (J. Soc. Chem. Ind. 1909, 28, 336), there is a relationship between the maturity of the grain and the gliadin content, the more fully ripened wheat containing the higher proportion.

Gluten may be estimated in flour as follows: 30 grams of flour are made into a dough with from 12 to 15 c.c. of water, and set aside for an hour. The dough is then worked between the fingers in a stream of running water to wash out the starch, being held over a muslin screen, so that any particles which are dropped can be recovered. Finally the gluten is worked vigorously between the fingers to remove the last traces of starch. With practice the washing can be carried out so as to occupy always the same time. The ball of gluten is then placed under water for an hour. It is next freed from excess of moisture by working between the hands and wiping off excess of water until the moment when the ball begins to stick: it is then removed to a little square of parchment paper, weighed, and dried for at least 24 hours at 100°. The ratio of the wet and dry weights gives the hydration ratio. Considerable information as to the strength of the gluten is gained by the feel both of the dough and of the gluten between the fingers. The method, though empirical, gives with practice very trustworthy results.

Marchadier and Goujon (J. Pharm. Chim.

1914, vii. 10, 191–202) have shown that the abnormal diminution in the percentage of coagulable gluten in wheat flour produced by mixing it with flour from buckwheat, barley, rice, maize, &c., is also produced by the admixture of inorganic substances, such as powdered talc, magnesia, or silica. This is not due to a variation in the ratio gliadin to glutenin, but to a variation in the sum of these two.

Germination, milling, preservation of the flour either in a moist state or in a humid atmosphere, and unfavourable meteorological conditions during the growth of the corn, produce a similar diminution in the percentage of coagulable gluten, due in this case to the conversion of glutenin into gliadin or *vice versâ*. It is suggested that the diminution in all these cases is due to a rise in the acidity of the flour under the conditions named, the coagulation of gluten being materially hindered by a very slight rise in the acidity.

It was at one time customary to test the quality of the gluten in an aleurometer. The wet gluten was placed in a tube provided with a piston, heated to a definite temperature (150°), and the amount of expansion read off. This test is of very little value.

As a check on the gluten estimation, the total nitrogen may be determined by Kjeldahl's method in the flour and in the crude dry gluten, and multiplied by 5·7 to express it as protein.

Gluten in the form of a light-brown powder, dried at a low temperature, is a commercial product, being used for the manufacture of bread and biscuits for diabetic patients: it usually contains from 3 to 5 p.c. of starch, and sometimes a great deal more, and should yield a very tough elastic dough when wetted.

In the commercial process the flour is made into a stiff dough, placed in open kneading machines, and kneaded with water. The starch goes into suspension, the starch milk being strained off periodically until gluten alone remains in the machine.

The open kneading machine most used for the process consists of a trough in which two kneading arms work in opposite directions.

In Germany wheaten starch factories are often run directly in connection with a bakery.

The flour is kneaded out as described and 60–75 p.c. pure starch obtained. The glutinous residues are then used for baking.

Westrup (Eng. Pats. 4028, 1908; 8337, 1909) proposes to test the strength of flours by making a ball of 15 grams flour and 7·5 grams of water, and placing this under a disc of plate glass, 3½ inches in diameter. A 200-gram weight is put on the glass for 30 minutes. The dough is pressed out, and, after hardening for 24 hours, the circumference of the flattened cake is measured by rolling it along a scale. Different flours are flattened to different extents.

Baine (Eng. Pat. 14770, 1909) puts a dough of standard proportions into a cylinder provided with a piston. As the dough rises, the piston is pushed up, an arresting mechanism prevents it dropping from the highest point reached, which can be read off later.

Neither of these methods appears to be of much practical value.

Gliadin. Wheat gluten was first separated into two constituents in 1819 by Taddei, who termed the alcohol soluble protein gliadin. Subsequently, Ritthausen thought gliadin to consist of three different proteins, but the researches of Osborne and others have made it clear that only one alcohol-soluble protein is present in wheat.

The alcohol-soluble protein of rye is apparently identical with that of wheat, and is therefore also termed gliadin. Other alcohol-soluble cereal proteins are the hordein of barley and zein of maize; these, however, are quite different from gliadin. Osborne has proposed to call this group *prolamins*.

The solubility of gliadin is a maximum in 70 p.c. ethyl alcohol: it is nearly insoluble in water and in absolute alcohol. When dehydrated with absolute alcohol and dried over sulphuric acid, gliadin is obtained as a colourless friable substance. As precipitated from dilute alcohol or water and dried, it is amorphous and transparent, somewhat resembling gelatin, but it is more brittle. It turns sticky with distilled water, and part dissolves, still more being dissolved on boiling. The addition of the smallest quantity of a mineral salt immediately precipitates it completely, either from aqueous or dilute alcoholic solution. The salts with acids or alkalis are freely soluble in water. They are precipitated unchanged on neutralisation.

Gliadin may be extracted both from gluten and from flour with 70 p.c. alcohol. The residue will no longer form a dough when wetted with water.

Gliadin has the composition C = 52·72 p.c., H = 6·86 p.c., N = 17·66 p.c., S = 1·03 p.c., O = 21·73 p.c., and gives 5738 calories per gram on combustion (Benedict and Osborne, J. Biol. Chem. 1907, 3, 119). The specific rotation in 70 p.c. alcohol is −92° (Mathewson, J. Amer. Chem. Soc. 1906, 28, 1482): the same author has determined the rotatory power in a number of solvents.

The total nitrogen, 17·66 p.c., is distributed as follows: as ammonia 4·33 p.c., basic 1·09 p.c., non-basic 12·17 p.c.

Osborne and Clapp (Amer. J. Physiol. 1906, 17, 231) have made a very careful determination of the products of hydrolysis of gliadin (*see also* Abderhalden and Samuely, Zeitsch. physiol. Chem. 1905, 44, 276). Their figures are as follows:—

	p.c.		p.c.
Glycine .	absent	Tyrosine .	1·20
Alanine .	2·00	Cystine .	0·45
Valine .	0·21	Lysine .	absent
Leucine .	5·61	Histidine .	0·61
Proline .	7·06	Arginine .	3·16
Phenylalanine	2·35	Ammonia .	5·11
Aspartic acid	0·58	Tryptophan	present
Glutamic acid	37·33		
Serine .	0·13	Total	65·80

The striking points in the composition are the absence of glycine and lysine and the small proportion of basic amino acids, the very large quantity of glutamic acid and the high proportion of ammonia and proline.

About 60 p.c. of the total sulphur in gliadin is converted into sulphide on boiling with sodium hydroxide.

Glutenin. The second protein of gluten is characterised by being insoluble in water, saline solutions, and alcohol, and remains after exhaustive treatment of gluten with these three solvents. When freshly prepared, it is soluble in 0·1 p.c. potassium hydroxide and 0·2 p.c. hydrochloric acid, and also in very dilute sodium carbonate and ammonia. After drying over sulphuric acid, it forms an amorphous greyish-brown powder somewhat less soluble in these reagents. It is precipitated on neutralisation. The only other cereal protein described, similar to glutein, is the oryzenin of rice (Rosenheim and Kajiura, J. Physiol. 1908, 36, liv), although it is probable that other seeds contain similar proteins. Osborne groups these as *glutelins.*

Glutenin has the composition, C 52·34 p.c. H = 6·83 p.c., N 17·49 p.c., S = 1·08 p.c. O = 22·26 p.c.; heat of combustion 5704 calories (Benedict and Osborne, J. Biol. Chem. 1907, 3 119). The nitrogen is distributed as follows: ammonia, 3·30 p.c; basic, 2·05 p.c.; non-basic, 11·95 p.c.

According to Osborne and Clapp, the products of hydrolysis are:

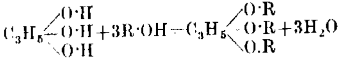
	p.c.		p.c.
Glycine .	0 89	Tyrosine .	4·25
Alanine .	4·65	Cystine .	0·02
Valine .	0·24	Histidine .	1·76
Leucine .	5 95	Arginine .	4·72
Proline .	4·23	Lysine .	1·92
Phenylalanine	1·97	Ammonia .	4·01
Aspartic acid	0 91	Tryptophan	present
Glutamic acid	23·42		
Serine .	0·74		59·68

[See the Discussion on Wheat, Brit. Assoc Report, Winnipeg, 1909, Supplement to J. Board of Agric. 1910, vol. 17, No 3; *see also* T. B. Osborne, Pflanzenproteine, Wiesbaden, 1910; Jago, Science and Art of Bread-making, London, 1911.]

E. F. A.

GLYCARBIN. Syn. for glyceryl carbonate.

GLYCERIN (*Glycerol, Glycyl alcohol, Propenyl alcohol* $C_3H_8O_3$ or $C_3H_5(OH)_3$) occurs in combination with fatty acids in all fatty oils and fats. Glycerin was discovered by Scheele, when preparing lead plaster from olive oil, and was termed by him '*principium dulce.*' The fatty oils and fats may be regarded as salts formed by the combination of fatty acids and glycerol, with the loss of three molecules of water. Glycerol being a trihydric alcohol, and consequently behaving like a trihydric base, is able to combine with three radicles of fatty acids, as is expressed by the following equation, in which R represents the acid radicle of any fatty acid:



$$C_3H_5\begin{cases}O\cdot H\\ O\cdot H\\ O\cdot H\end{cases}+3R\cdot OH=C_3H_5\begin{cases}O\cdot R\\ O\cdot R\\ O.R\end{cases}+3H_2O$$

This equation, when read from right to left, symbolises the process of saponification of fats, and expresses the fact, that by the addition of water (under suitable conditions) to the neutral glycerides, the latter are resolved into three molecules of fatty acids and one molecule of glycerol (*see* SAPONIFICATION). From the right side of the equation it follows that glycerol does not exist as such in the fatty oils and fats, but that it is formed by the assimilation of three molecules of water. Hence the sum of the weight of the fatty acids and glycerol is always greater than the weight of the original fat employed. The excess over 100 p.c. may be gathered from the following table by adding up the numbers given in column 4, and deducting 100 from that sum (*see* column 5).

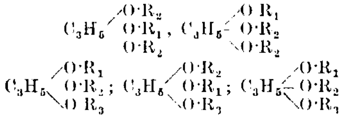
Owing to this complete analogy between the formation of a tribasic salt and a triglyceride, the natural triglycerides are also termed 'neutral glycyl esters.'

The triglycerides of the most frequently occurring fatty acids are collated in the following table, in which their chemical formula and molecular weights are given, as also th quantities in p.c. of fatty acids and glycero resulting from saponification of 100 parts of th glycerides:—

1	2	3	4		5	6
Glyceride	Formula	Molecular weight	Products obtained on saponification of 100 parts		Excess over 100 parts	Chief sources
			Fatty acids	Glycerin		
			p.c.	p.c.	p.c.	
Glyceryl tributyrate (Butyrin)	$C_3H_5(O\cdot C_4H_7O)_3$	302	87·44	30·40	17·90	Milk fats
„ tricaproate (Caproin)	$C_3H_5(O\cdot C_6H_{11}O)_3$	386	90·15	23·96	14·11	Milk fats, cocoa-nut oi palm -nut o
„ tricaprylate (Caprylin)	$C_3H_5(O\cdot C_8H_{15}O)_3$	470	91 91	19·58	11 49	„ „ „
„ tricaprate (Caprin) .	$C_3H_5(O\cdot C_{10}H_{19}O)_3$	554	93·14	16·67	9·81	„ „ „
„ trilaurate (Laurin) .	$C_3H_5(O\cdot C_{12}H_{23}O)_3$	638	94·04	14·42	8·46	Laurel oil, cocoa-nut oi palm-nut oil, dika f
„ trimyristate (Myristin)	$C_3H_5(O\cdot C_{14}H_{27}O)_3$	722	94·75	12·74	7·49	Myristica fats
„ tripalmitate (Palmitin)	$C_3H_5(O\cdot C_{16}H_{31}O)_3$	806	95·29	11·42	6·71	Palm oil, Chinese veg table tallow, Japan w
„ tristearate (Stearin) .	$C_3H_5(O\cdot C_{18}H_{35}O)_3$	890	95·73	10·34	7·07	Cacao butter, tallow
„ trioleate (Olein) .	$C_3H_5(O\cdot C_{18}H_{33}O)_3$	884	95·70	10·41	6·11	Olive oil, lard oil, tallo oil
„ trilinolate (Linolin) .	$C_3H_5(O\cdot C_{18}H_{31}O)_3$	878	95·67	10·4[illegible]	6·15	Drying and semi-dryin oils
„ trilipolenate (Linolenin)	$C_3H_5(O\cdot C_{18}H_{29}O)_3$	872	95·63	10·55	6·18	Drying oils
„ triclupanodonate (Clupanodonin) . .	$C_3H_5(O\cdot C_{18}H_{27}O)_3$	866	95·61	10·62	6 23	Marine animal oils
„ triricinoleate (Ricinolein)	$C_3H_5(O\cdot C_{18}H_{33}O_2)_3$	932	95·93	9·87	5·80	Castor oil
„ triarachidate (Arachin)	$C_3H_5(O\cdot C_{20}H_{39}O)_3$	974	96·09	9·45	5·54	Earth-nut oil
„ trierucate (Erucin)	$C_3H_5(O\cdot C_{22}H_{41}O)_3$	1052	96·39	8·7[illegible]	5·13	Rape oils

From the above formulæ it appears that glycerol is regarded as a trivalent, or triatomic alcohol, containing the radicle C_3H_5 in combination with three OH groups. Hence, glycerol bears the same relation to ordinary ethyl alcohol as orthophosphoric acid bears to nitric acid. Just as tribasic phosphoric acid forms three distinct classes of salts, with three different proportions of the same base, so does glycerol form three distinct classes of esters, viz. monoglycerides, diglycerides, and triglycerides (*see* OILS, FIXED, and FATS). And just as phosphoric acid may combine with two or three different bases to form two different classes of tribasic salts, so does glycerol lead to different classes of triglycerides. Each triglyceride enumerated in the foregoing table must be considered as glycerol in which all three hydrogen atoms of the three OH groups are replaced by one and the same radicle of fatty acid. Such glycerides are termed *simple triglycerides*. If, however, the three hydrogen atoms are replaced by two or three different fatty acid radicles, *mixed glycerides* are obtained.

Should a triglyceride contain two different fatty acid radicles, two isomeric triglycerides may be expected; and in the case of a triglyceride containing three different acid radicles, three isomerides may be expected. This is explained by the following formulæ:—



$$C_3H_5\begin{cases}O{\cdot}R_2\\O{\cdot}R_1\\O{\cdot}R_2\end{cases},\quad C_3H_5\begin{cases}O{\cdot}R_1\\O{\cdot}R_2\\O{\cdot}R_2\end{cases}$$

$$C_3H_5\begin{cases}O{\cdot}R_1\\O{\cdot}R_2\\O{\cdot}R_3\end{cases};\quad C_3H_5\begin{cases}O{\cdot}R_2\\O{\cdot}R_1\\O{\cdot}R_3\end{cases};\quad C_3H_5\begin{cases}O{\cdot}R_1\\O{\cdot}R_2\\O{\cdot}R_3\end{cases}$$

It was formerly assumed that the natural fats consisted of simple triglycerides; modern researches, however, have made it extremely likely that simple triglycerides occur in nature, as a rule, in small quantities only, and that natural oils and fats are composed chiefly of mixed glycerides. Thus, for instance, in tallow, only a few p.c. of tristearin have been found; hence tallow must be assumed to consist mainly of mixed glycerides.

A considerable number of mixed glycerides have been already isolated from such natural oils and fats as tallow, cacao butter, Borneo tallow, &c. The mixed glycerides of most frequent occurrence which have been isolated hitherto are *oleodipalmitin*, *stearodipalmitin*, *oleopalmitostearin*, *palmitodistearin*, *oleodistearin*, and *dioleostearin*.

Glycerin has also been found, in the free state, in the blood and in fermented alcoholic liquors. Pasteur has shown that glycerin is a constant product of the alcoholic fermentation of sugar; hence it is a natural constituent of beer, wine, &c. 100 parts of sugar produce 3·5 parts of glycerin. Until a few years ago these latter sources of glycerin were of no commercial importance, but the increasing value of glycerin has made it profitable to recover even this small proportion, and several processes have been devised for treating the *vinasses* from distilleries. For example, in Barbet's process (Fr. Pat. 449961 of 1912) the material is concentrated, mixed with calcined plaster and kieselguhr, and the glycerin distilled under reduced pressure, while caramelisation is prevented by the action of scrapers within the retort. In another process (Eng. Pat. 27300 of 1912) the *vinasses* is dried, treated with acid, and the glycerin extracted by means of solvents such as alcohol. Increased quantities of glycerin are obtained from molasses by fermentation with *Saccharomyces ellipsoideus* (var. Steinberg) in presence of sodium carbonate and ammonium chloride at a temperature of 30°–32°, when from 20 to 25 p.c. of the sugar is converted into glycerin, and the greater part of the remainder into alcohol and carbon dioxide. The investigations of Lüdecke on the production of glycerin on an industrial scale from the fermentation of sugar led to a practical process worked out by Connstein and Ludecke, which was employed to a considerable extent in Germany during the great war. The process is based upon the fact that the percentage of glycerin is increased if the fermentation proceeds in presence of alkaline substances, particularly sodium sulphite, whereby it was possible to obtain 20 parts of purified glycerin, 27 parts of alcohol, and 3 parts of aldehyde from 100 parts of sugar. After removal of the yeast by filtration and of the alcohol and aldehyde by distillation, the bulk of the salts present are precipitated by calcium chloride and then by sodium carbonate, the liquid being afterwards neutralised with hydrochloric acid and filtered from the sludge; concentration and distillation yield a glycerin suitable for technical purposes (J. Soc. Chem. Ind. 1919, 38, 287; R. Schweizer, Chim. et Ind. 1921, 6, 149).

The synthetic preparation of glycerin, although it has been made the subject of several patents, has as yet hardly passed beyond the theoretical stage.

Glycerin is obtained on a large scale in the several saponification processes which are practised in candle and soap works (*see* SAPONIFICATION). According to the process by which the commercial product 'crude glycerin' is obtained, we differentiate in commerce the following five qualities of crude glycerin, viz.: (1) crude saponification glycerin; (2) crude distillation glycerin; (3) Twitchell crude glycerin; (4) fermentation crude glycerin; (5) soap lye glycerin, or soap crude glycerin.

In the stearine candle and soap industries, glycerin is obtained as a dilute aqueous solution, which contains various impurities, the nature and quantity of which depend on the manufacturing processes themselves. The purest raw material results from saponification by means of lime in open vessels; hardly inferior to this is the glycerin obtained by 'autoclaving.' Less pure is the raw material recovered from the 'acid saponification process,' 'Twitchell's process,' and the 'ferment process.' The crude glycerin obtained from soap lyes, notwithstanding its high proportion of inorganic salts, may, on the one hand, surpass in purity (*i.e.* as regards the amount of organic impurities) the crude material from the last-named processes; but, on the other hand, it may be very impure if fats and oils of low quality have been saponified by means of black-ash lyes, as was done until a few years ago in Lancashire and in Marseilles. Modern processes of refining have, however, overcome a number of difficulties caused by the several impurities, so that *e.g.* chemically pure glycerol from good soap lyes cannot be distinguished from chemically pure glycerol obtained by lime saponification. Crude glycerins further vary as regards quality in accordance with the care exercised in the manufacture. Crude glycerins obtained from the acid saponification, the Twitchell, and the fermentation processes, retain very tenaciously some organic impurities which hitherto seem to have defied all attempts to remove them, as the writer has ascertained in the case of a number of 'chemically pure' glycerols originating from these processes.

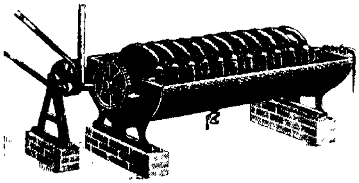


FIG. 1.

1. **Crude saponification glycerin.** This glycerin represents the best quality of crude glycerin. It is obtained from the 'sweet water' of the autoclave process (*see* SAPONIFICATION) and as a by-product in the process of soap making by double decomposition.

The proportion of glycerol in the 'sweet waters' varies from 6 to 16 p.c. The metallic oxides contained in the 'sweet waters' are neutralised, and the filtered solution is concentrated by means of steam, either in a Wetzel pan (Fig. 1) or, as is done in modern works, in a vacuum evaporator of a type identical with or similar to those shown in Figs. 2, 3. According to the quantity of salts which separate when the bulk of water has been driven off, a vacuum evaporator either of the type A or type B (Fig. 4) is used. The evaporation is carried on until the crude glycerin contains about 85–90 p.c. of glycerol. Its sp.gr. is then from 1·240 to 1·242, corresponding with the commercial brand of '28°Bé saponification crude' or 'candle crude glycerin.' The colour of this glycerin varies from yellow to dark-brown; its taste is sweet. With basic lead acetate, it gives but a slight precipitate. By refining this crude glycerin with charcoal, a 'refined' glycerin (used for a number of commercial purposes) is obtained. This crude glycerin contains up to 0·3 p.c. of ash, chiefly calcium (or magnesium or zinc) sulphate, and only small quantities of organic impurities.

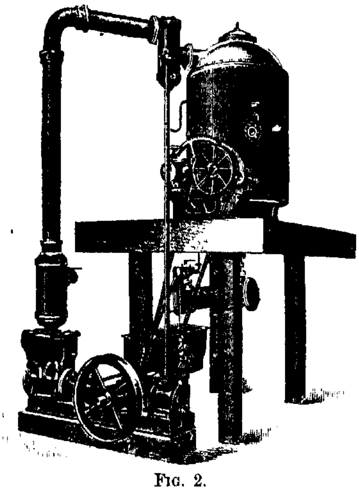


FIG. 2.

This crude glycerin is valued on the percentage of pure glycerol, of ash, and of organic impurities.

The 'sweet water' obtained in the process of soap making by double decomposition is treated in the same manner as described above, and yields a good 'saponification crude,' which is equal in quality to a 'candle crude glycerin,' provided that the original fatty matter was of good quality. Since this process is used in small works only, where chiefly low-quality greases are worked up, the crude glycerin thus obtained is apt to contain a considerable amount of organic impurities, so that it is liable to ferment when stored. Within the author's experience, such crude glycerins did ferment, thus showing that the organic substances in low-class grease are not destroyed by treatment with lime. In the course of the fermentation, trimethyleneglycol is formed. This crude glycerin is also high in proportion of ash (the author found even as much as 1·77 to 5 p.c. of ash), whereas the respective proportions of glycerol were 84·3 and 77·1 p.c.

A typical sample of high quality examined by Grimwood (1918) had: sp.gr. 1·2455; glycerol, 89·7 p.c.; ash, 0·55 p.c.; and organic residue, 0·57 p.c.

2. **Crude distillation glycerin.** This kind of crude glycerin is obtained from the acid water resulting in the so-called acid saponification processes (*see* SAPONIFICATION). It is termed in commerce 'crude distillation glycerin' for the reason that the fatty acids obtained by this process must be distilled to yield candle material. The dilute glycerin waters ('sweet waters') are worked up in the same manner as described under 'crude saponification glycerin,' but owing to the large amount of sulphuric acid used in the process, a considerable quantity of salts remain in solution after the mineral acid has been neutralised with lime. As the concentration of the solution proceeds, especially when the thickened liquor approaches the sp.gr. of 1·240, calcium sulphate, which is no longer held in solution, separates out, and is deposited on the heating surface of the evaporating apparatus in the form of a hard crust, which rapidly diminishes the evaporative power of the steam, unless the calcium sulphate is removed.

Hence, such tube evaporators as are represented by vessel B (Fig. 4) are useless for concentrating the dilute solution, and a type of evaporator must be employed which permits the heating surface to be continuously scraped so as to keep it clean. An evaporator of this kind, designed by the author, is shown in Fig. 2, the inner construction of which is exemplified by Fig. 3.

The finished crude distillation glycerin contains considerable proportions of calcium sulphate, inasmuch as the solvent power of glycerol for calcium sulphate (*see* below) is still further increased by the organic impurities which the crude glycerin retains. The ash of this kind of crude glycerin rises to as much as 2 and even 3·5 p.c. The amount of organic impurities is greater than in crude saponification glycerin, and it may rise to even 2 p.c., the amount depending on the lack of care exercised in the manufacturing process. The colour of this crude glycerin is usually pale-yellow; its taste is sharp and astringent, and when rubbed between the hands it emits an unpleasant smell. On adding basic lead acetate, a voluminous precipitate is obtained; hydrochloric acid produces a turbidity, due to the presence of fatty acids.

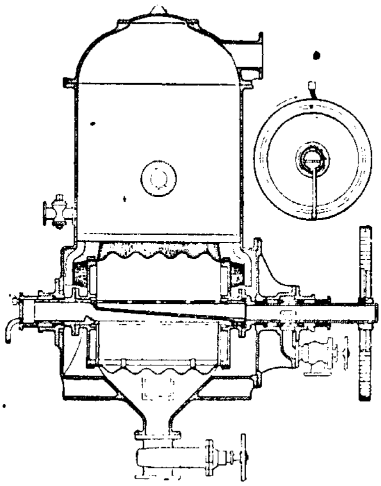


FIG. 3.

This crude glycerin has the sp.gr. 1·240–1·242. As a rule, it contains from 84 to 86 p.c. of glycerol. The trade term for this kind of glycerin is 'crude distillation glycerin, 28°Bé.'

3. **Crude glycerin from the Twitchell process.** This kind of crude glycerin is obtained from the acid water resulting in Twitchell's saponification process (*see* SAPONIFICATION). The sweet waters are treated with lime or barium hydroxide or barium carbonate, so as to precipitate the dissolved sulphuric acid as completely as possible. The purified liquors are concentrated up to a sp.gr. of about 1·24 or more, in the same manner as described under the two preceding headings. The quality of this crude glycerin varies considerably with the quality of the fatty material from which it has been obtained. If the raw material is of good quality, the glycerin is fairly good; but even in that case, owing to the high amount of ash it contains, and owing to its unpleasant taste, it is valued at a somewhat lower price than is crude candle glycerin. By way of example, the following analysis made by the author, may be given: sp.gr. 1·239; glycerol, 84·8 p.c.; ash, 0·52 p.c. A typical sample analysed by Grimwood (1918) had: sp.gr. 1·2453; glycerol, 87·0 p.c.; ash, 1·1 p.c.; and organic residue, 1·4 p.c. Since the Twitchell saponification process is best adapted to low-class material (such as greases), the glycerin obtained from such material contains so considerable an amount of organic impurities that it cannot be refined by itself, even for the production of dynamite glycerin. Each special make of such glycerin must therefore be valued on the basis of the impurities it contains.

4. **Fermentation crude glycerin** (*see* SAPONIFICATION). The sweet water from the process of hydrolysis by means of enzymes is rich in proteins and other organic impurities. In addition to the usual treatment described above, it must be filtered over char, which retains the bulk of the proteins and other organic impurities. Nevertheless, a certain amount is still retained; consequently, the finished crude is not only dark in colour, but has also a very unpleasant smell and taste, even if the glycerin be made from good raw material, such as refined cotton-seed oil or refined linseed oil. In the infancy of the process, the crude glycerin obtained thereby was practically unusable. In consequence of improvements, the amount of impurities has been considerably reduced, so that a sample examined in the author's laboratory gave the following somewhat favourable results: sp.gr. 1·2369; ash, 0·49 p.c.; organic impurities (proteins, &c.), 1·54 p.c. But the difficulties have not yet been sufficiently surmounted to make the process satisfactory, and it is still but little used. The last two kinds of crude glycerin are difficult to refine (by the usual process of distillation) and must be mixed in the glycerin still with better kinds of crude glycerin.

5. **Soap lye glycerin, Soap crude glycerin, Soap crude.** Since Chevreul established the constitution of fats and oils, it has been known that the spent soap lyes, resulting in the manufacture of soap, contain, if not the whole, a very large proportion of the glycerol, combined originally with fatty acids in the oils and fats which had been converted into soap in the soap pan. During the first half of last century, no attempt had been made to recover the glycerol from those lyes, not only on account of the difficulty attending this operation, but also for the reason that the small demand for glycerin then ruling in the market could be readily satisfied by the candle makers' crude glycerin. When, at the end of the seventies of the last century, a great demand for nitroglycerin ('dynamite') sprang up, attention was drawn forcibly to this source of glycerin, and serious endeavours were made to recover the hitherto wasted product. Although as early as 1858, H. Reynolds had patented the main features of a process of recovery, features which essentially reappeared in all subsequent processes, yet serious failure at first attended all attempts at the recovery of glycerin, on account of the considerable amount of impurities in the spent lyes, and most prominently on account of the large amount of dissolved salts. Modern processes, especially improvements in apparatus on the one hand, and the rapidly growing employment in the soap industry of

caustic soda of the highest purity, tended to evolve a process which is now worked with more or less success in all the large soap works, not only of Europe and America, but also of Australia, Africa, India, and New Zealand. The earliest successful attempts to recover glycerin from soap lyes were made in English soap works, where the largest quantities of oils and fats were worked up in the largest soaperies of the world; the working up of the soap lyes for crude glycerin may be said to have established its success in Great Britain towards the middle of the 'eighties of the last century. Since that time, crude glycerin recovered from soap lyes, 'soap crude glycerin,' has established its great importance in the world's commerce.

The lyes obtained in the soap-making process by boiling oils and fats in an open pan with caustic soda contain practically all the glycerol which the natural oils and fats are capable of yielding. According to the manner in which the 'changes' are worked up (*see* SOAP), the spent lyes contain from 5 to 8 p.c. of pure glycerol. In addition to glycerol, the spent lyes hold in solution the common salt used in 'cutting' the soap, and also small amounts of free caustic soda, sodium carbonate, soap, and organic impurities. The less free caustic soda, sodium carbonate, and organic impurities the lyes contain, the more readily can the process of recovery and purification be carried out. In case impure caustic soda lyes have been used (*see* above), the spent soap lyes contain, in addition to the substances enumerated above, thiocyanates, sulphides, thiosulphates, cyanides, and ferrocyanides. These impurities were present in the crude (black-ash) lyes, which were used up to a few years ago to a large extent in the Marseilles district. The difficulties caused thereby in the recovery of crude glycerin have led, favoured by the establishment of Solvay's soda works in that neighbourhood, to the almost complete abandonment of black-ash lyes, so that even in Marseilles the vast majority of soaps are prepared with pure caustic lyes. The exact treatment of the lyes in a soap works depends on the state of purity of these lyes, and has, as its object, the removal or destruction of the albuminous, resinous, and soapy matters present in the lyes. This is done by various additions, such as lime or hydrochloric acid, or salts of aluminium and iron, which precipitate foreign substances, so that they can be filtered off, whereupon the purified lyes are neutralised and become ready for concentration. The purified lyes are boiled down in fire-heated vessels, which are of a conical shape, so that the salt, as it separates, slides down into a vessel fixed to the bottom of the pan, whilst rotating gear keeps the heating surface free from incrustation. Such vessels, although in large works considered antiquated, are still being used and even introduced in smaller works, where the amount of water available is limited or where water is very dear. In the case of large works, the lyes are usually evaporated *in vacuô*. The first concentration of the lyes to the 'salting-point' (at which salt commences to separate) is considered to have been completed when the lyes have reached a sp.gr. of 44°Tw. at 15·5°C. The percentage of glycerol in these lyes then usually amounts to 10–16 p.c. If evaporation were carried on beyond this 'salting-point' in a tube evaporator, the separated salts would deposit on the tubes, and thus soon prevent the evaporation from proceeding to the desired stage. The author has frequently seen tube evaporators which, after a couple of days' working, had become so heavily encrusted with salts that the evaporator had to be stopped and 'laid off' for cleaning. A large number of patents has been taken out, with a view to preventing the settling down of the salts on the evaporator tubes. Lewkowitsch overcomes this difficulty by providing the evaporator with suitable stirring and scraping arrangements, which remove the salts as they separate, the salts falling down into a vessel (of any desired shape) which can be shut off from the vacuum evaporator, and emptied at will under ordinary pressure. After removal of the salt, the vessel is exhausted and again connected with the evaporator. An evaporator of this type is shown in Fig 2. The construction of the rotating heating surface is typified by Fig. 3. In these evaporators, the soap lyes can be evaporated from their dilute stage beyond the 'salting-point,' the salt which falls out being removed by using, at given intervals, the vessel fixed to the outlet of the evaporating pan. This vessel, as has been pointed out already, can be emptied while the contents are kept continuously boiling. In large installations, the lyes are concentrated in double, or triple, or quadruple effect vacuum apparatus. A double effect, designed by Lewkowitsch on the same principle as Fig. 2, is illustrated by Fig. 4.

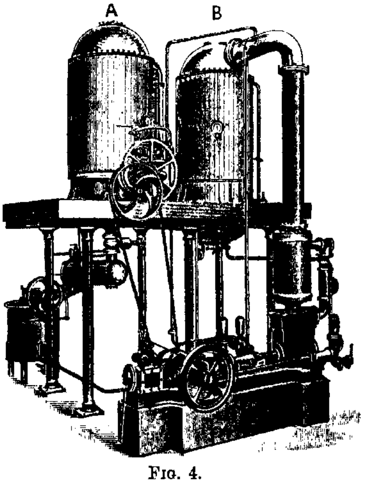


FIG. 4.

This figure shows a combination of a tube evaporator, B, with an evaporator as illustrated by Fig. 2. The first preliminary concentration up to the 'salting-point' is carried out in vessel B, whilst the further concentration takes place in vessel A. The salt which separates out during the process of concentration is collected in the vessel shown underneath A, and is removed at fixed times, and washed in the washing machine shown in the illustration. The salt is washed first with purified lyes of low percentage of glycerol, and finally with water to remove the glycerin from the salt. The salt itself is recovered in such purity that it can be used immediately in the soapery in place of fresh salt (*see* Soap).

The glycerin solutions are boiled *in vacuô* until the crude glycerin has reached a sp.gr. of 1·3. The progress of concentration is controlled by the sp.gr. test, or, equally well, by taking out samples and ascertaining the boiling-point in a porcelain dish, by means of a thermometer, while the contents of the dish are kept stirred, so that the salt may not cause bumping of the contents or cracking of the dish. The glycerin has reached the sp.gr. of 1·3 and the percentage required by commerce, if the boiling-point is 150°. The crude glycerin then contains 80 p.c. of pure glycerol, and about 10 p.c. of salts, the remainder consisting of water and a small amount of organic impurities. If the concentration is carried a little further, crude glycerin, containing as much as 86 p.c. of glycerol, can readily be obtained.

The proportion of organic impurities in soap-lye glycerin varies considerably, depending on the process of purification and the care of the operator. Some commercial soap crude glycerins contain less than 1 p.c. of organic impurities (thus representing a better quality glycerin than 'crude distillation glycerin,' crude glycerin from the 'Twitchell process,' and crude glycerin from the 'fermentation process'). Other specimens of crude glycerin, again, contain large quantities of impurities, consisting of fatty acids, rosin acids, and of albuminoid substances, gelatin, and hydrocarbons (from bone fat), and also trimethyleneglycol in the lyes resulting from bone fat which has been allowed to ferment. In the distillates from such impure glycerins, the author even found organic bases, amongst which he identified picoline and lutidine.

The following analyses by Grimwood show the composition of typical samples of crude glycerin in 1917–1918:—

	Sp.gr.	Glycerol p.c.	Ash p.c.	Organic residue p.c.
High quality .	1·3097	85·8	9·33	1·68
Low quality .	1·2980	77·2	10·63	3·61

The colour of 'salt crude glycerin' is pale-yellow to brown, or almost black, according to its purity. The taste of good 'soap crude' is sweet, qualified, of course, by that of the common salt contained therein. Impure samples have a most unpleasant garlic-like taste, even if sulphides be absent. This is specially characteristic of the lyes obtained in the Marseilles district (due to the use of 'sulphur' olive oil).

Soap-lye glycerin can be rapidly distinguished from the crude glycerins described above by the large proportion of common salt which it contains (heavy precipitate with silver nitrate solution) and by its high sp.gr.

soap-lye glycerin containing considerable quantities of sulphides, thiosulphates, or sulphites, is almost valueless to the refiner of crude glycerin.

Considerable quantities of crude glycerin, especially crude saponification glycerin, are used in the arts for various purposes, *e.g.* in the manufacture of inks. By far the largest quantities of crude glycerin are, however, purified by distillation, and thereby converted into 'distilled glycerin.' In commerce, two kinds of distilled glycerin are differentiated, distilled glycerin for making nitroglycerin (dynamite), 'dynamite glycerin,' and chemically pure glycerin, sometimes termed 'twice-' or 'treble-distilled glycerin.'

Distilled glycerins are obtained, as the name implies, from crude glycerin by distillation. The distillation is carried out, either under ordinary pressure or in a vacuum. In either case the distillation is supported and accelerated by the aid of steam. At present vacuum distillation, coupled with superheated steam, is the combination mostly in vogue. Some manufacturers work off a certain amount (depending on the size of the still) of crude glycerin in one batch. Other manufacturers resort to continuous distillation, the still being fed as the glycerin distils off.

The successful distillation of crude glycerin does not so much depend on the kind of still and condensers used as on the skill and care of the operator. A considerable number of special apparatus have been patented, and are still being patented, but owing to the fact pointed out, viz. that success depends more on attention to details than on the particular apparatus employed, the details of the *modus operandi* in conducting the distillation are considered valuable secrets.

Space does not permit a complete reference to the patent literature or to the illustrations accompanying it. It may therefore be generally stated that some inventors introduce details which neither contribute to cheapening the process nor permit the realisation of the refinements claimed. Some of the apparatus embody a faulty principle, inasmuch as not only is complete purification not effected, but even partly purified distillates are contaminated with the impurities driven off from a partially purified batch. Here it may suffice to illustrate in Fig. 5 a glycerin distillation plant which the author designed for the distillation of crude glycerins, both of 'saponification crude' and 'soap crude.' The still shown is provided with an arrangement for withdrawing the salts as they separate out. The contents of the still are heated by means of open superheated steam, which carries off the vapours of glycerin into a battery of condensing columns. Between the latter and the still itself is inserted a catch box in which the heaviest portions are condensed, while small amounts of sodium chloride, which is carried over mechanically with the steam, are simultaneously deposited. From the end of the battery of columns a connection leads to a vacuum pump, the distillation being carried out *in vacuô*. The glycerin vapours, with varying amounts of water, condense in the several columns. In the first columns little water condenses; thus the strongest glycerin, of sp.gr. 1·25, is obtained therein. The following columns yield weaker glycerin liquors which, in the end column, are so dilute that the then escaping vapours are practically free from volatilised glycerin. The distillates are drawn off *in vacuô*, sampled and graded according to their sp.gr. In the figure, the vessels into which the glycerin is drawn off are partly shown.

It depends solely on the mode of working—especially in the case of soap-lye glycerin—as to whether one distillation will suffice to obtain a satisfactory product for nitrating purposes, or whether the once distilled glycerin must be redistilled. In case the distillation has not been conducted carefully, the once-distilled glycerin is so strongly contaminated with sodium chloride and organic impurities (volatile fatty acids and even polyglycerols), that a second distillation becomes imperative.

The distilled glycerin liquors collected from the columns are treated with char, if required, in order to remove some organic impurities, and, at the same time, to clarify the glycerin and improve its colour. The collected and filtered glycerin liquors are finally concentrated in a vacuum evaporator, up to the desired sp.gr. For the purposes of dynamite glycerin, the sp.gr. must be at least 1·261 at 15°. Other commercial qualities of distilled glycerin need only be concentrated to a sp.gr. of 1·250 or 1·240, as the case may be. The dynamite glycerin quality is used exclusively for purposes of making nitroglycerin. Other qualities of distilled glycerin, especially those of sp.gr. 1·250 and 1·240, are used for various purposes in the arts, such as for filling gas meters and hydraulic jacks, in the manufacture of ink, waterproof paper, toilet soaps, 'sizes' for textiles, and for the production of plastic masses, such as printing rollers, hectograph mass, &c. The bulk of the distilled glycerin is, however, employed in the manufacture of high explosives, such as dynamite, blasting gelatine, cordite, &c.

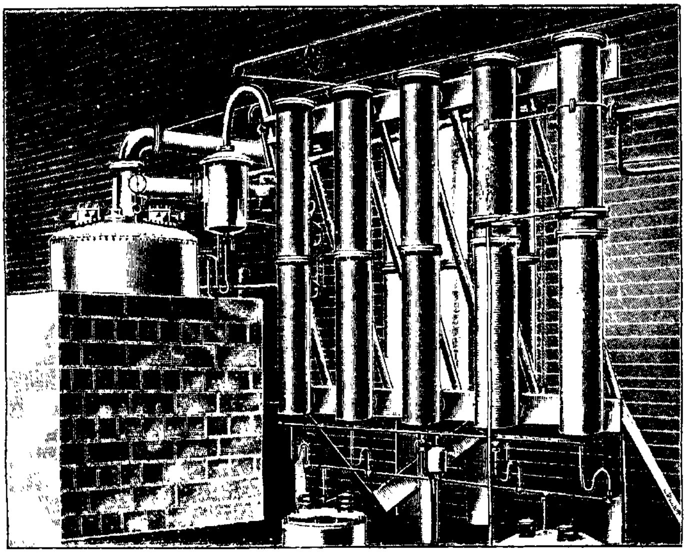


Fig. 5.

The yield obtainable from crude glycerin depends, just like the distillation itself, on the care of the operator. The losses incurred by faulty methods are large, and range, within the knowledge of the author, from as much as 15 to even 40 p.c. A large proportion of the loss is due to destruction of glycerol with the formation of volatile acids and acroleïn on the one hand, and to the formation of polyglycerols on the other hand. The polyglycerols which are formed in the course of distillation should remain in the still itself, and are found with the still residue (*see* below, *Glycerin foots*).

The commercial 'distilled glycerins' vary in colour from yellow to white; they also vary in their content of glycerol according to their sp.grs., which range, as a rule, between 1·220 and 1·260. Glycerin, purified by distillation, should contain a very small amount of ash only; thereby distilled glycerins are easily distinguished from crude glycerins.

The residues ('*glycerin foots*') remaining in the still, in the case of those crude glycerins which contain small proportions of ash (*see* above, *Crude glycerins*, 1, 2, 3, 4), consist chiefly of polyglycerols and of notable amounts of salts, as the mineral matters originally contained in the crude material naturally accumulate in the residues. These residues are used in the manufacture of shoe blacking. Claessen proposed to employ them also in the production of plastic masses, such as printing rollers, hectograph masses, sizes for textiles, and for waterproofing paper.

The still residues from soap lye crude contain much larger amounts of salts than those described above. The residues obtained in the *course of distillation* retain such considerable amounts of glycerol in addition to polyglycerols, salt, sodium carbonate, sodium acetate, and sodium salts of other organic non-volatile acids, that the accumulated residues are worked up for the recovery of glycerin. They are boiled up with water, and dilute hydrochloric or sulphuric acid is added to decompose the sodium carbonate and the organic salts. The organic non-volatile acids collect on the surface of the liquid as a resinous mass, which is removed in any suitable manner. The liquor is then filtered and concentrated separately, or is mixed with the ordinary soap lyes. As during the concentration of these liquors, acetic acid is volatilised, it is advisable to concentrate the lyes and distil the recovered crude glycerin separately.

The distilled glycerins described above contain, as a rule, amounts of impurities, which although small, are yet sufficiently large to forbid the employment of those distilled glycerins for pharmaceutical and dietetic purposes. The 'distilled glycerins' must therefore, as a rule, be subjected to a second distillation. If this distillation be carried out with sufficient care, the distillates give, after concentration and treatment with char, the chemically pure glycerin of commerce

At a time when the art of preparing chemically pure glycerin was not so far advanced as it is at present, some chemically pure glycerin was manufactured by allowing glycerin to crystallise, and centrifugalising the crystals, whereby the impurities were removed with that portion of glycerin which melted in the centrifugal machine. This process has, however, been abandoned, not only on account of its costliness, but also on account of the inferiority of the product as compared with the best brands of chemically pure glycerin obtained by careful distillation, as it was found that the crystals were apt to occlude impurities.

The statements found in chemical literature that glycerin only crystallises at −40°, must be corrected, in so far as glycerin, exposed for a long time to a low temperature (−5° or −10°), will gradually crystallise. Thus the author frequently found in very cold winters that glycerin, even glycerin of 'dynamite quality' which had been left undisturbed for some prolonged time, had crystallised.

Electro-osmotic processes of decolorising and purifying glycerin have been patented (Eng. Pats., 144,727, 145,046, 146,865, 1920).

Chemically pure glycerin is obtainable in commerce in the following 'strengths' (concentrations): chemically pure glycerin of 1·24 sp.gr., chemically pure glycerin of 1·25 sp.gr., and chemically pure glycerin of 1·26 sp.gr.

The chemically pure glycerin of the highest sp.gr. approaches, as nearly as is possible for a product made on a large scale, the chemical substance glycerol.

Glycerol (pure glycerin) is an odourless, colourless, viscid liquid, having an intensely sweet taste. The preparation demanded by the Pharmacopœias of different countries is the purest commercial article, which consists practically of glycerol, containing a very small amount of water. Glycerol is optically inactive, and is neutral to indicators. On exposure to an intense cold for a prolonged time, it crystallises in rhombic crystals, melting at 20°. With the help of a few crystals, large quantities of glycerol can easily be solidified at the temperature of the freezing-point of water.

Glycerin is oily to the touch, and produces on the skin, especially on the mucous membrane, the sensation of heat, due to its absorbing moisture from the tissues. The water-absorbing power of glycerin is so great that, on exposure to the atmosphere, it takes up as much as 50 p.c. of its own weight of water.

The sp.gr. of pure glycerin has been determined by several observers, whose statements do not agree, owing, no doubt, to the difficulty of removing the last traces of water. The most trustworthy values are the following :—

$$\text{sp.gr. } 15^\circ/15^\circ = 1{\cdot}26468\text{ ;}$$
$$\text{sp.gr. } 17{\cdot}5^\circ/17{\cdot}5^\circ = 1{\cdot}2620.$$

Kailan (Zeitsch. anal. Chem. 1912, 51, 81) obtained values of 1·26414 at 15°/4°, and 1·26082 at 20°/4°, which are in close agreement with those recorded by other chemists. The relationship between the sp.gr. and temperature is shown in the following formula (Kailan) :—

$$\text{Sp.gr. at } t^\circ/4^\circ = 1{\cdot}26413 + (15-t)0{\cdot}000632.$$

Provided a specimen of chemically pure glycerin satisfies the qualitative tests described below, the proportion of glycerol in it can be found by merely determining the sp.gr. of the sample. The percentage can also be obtained, approximately, from the refractive index of the glycerin. The table (p. 438) by Skalweit (Repertor. d. Analyt. Chemie, 5, 18) gives the sp.grs. and refractive indices, for the sodium ray, at 15°, of mixtures of glycerol and water in various proportions.

Other tables for the sp.gr. and the refractive indices of glycerol solution are given in Lewkowitsch's Chem. Technology of Oils, &c. Lenz states that the observations of the several observers agree amongst each other within a few units of the fourth decimal, whilst the differences in the refractive indices, corresponding to 1 p.c. of glycerol, amount to 13·5 units of the fourth decimal. By reference to the above table, the percentage of glycerol in a sample can therefore only be determined accurately to 0·5 p.c. (*cf.* Grün and Wirth, Zeitsch. angew. Chem. 1919, 32, 59). Bosart (J. Ind. Eng. Chem. 1921, 13, 944) has shown that Gerlach's table of sp. gr. at 15° is sufficiently accurate for technical purposes, but that his table of values at 20° is inaccurate.

Where the volume of glycerin is not enough to permit the accurate determination of its sp.gr., the refractive index can be ascertained with the aid of Abbe's refractometer. Zeiss's immersion refractometer has also been applied to the determination of dilute glycerin solutions ; but it should be noted that the immersion refractometer (which is used extensively for the determination of alcohol in beer and other fermented liquors) does not permit more concentrated solutions to be tested than those containing 26 p.c. It is not permissible to dilute concentrated glycerin with a known amount of water to a lower percentage, and then determine the refractive index, inasmuch as contraction takes place on mixing glycerin with water.

Glycerin boils under 760 mm. pressure at 290°, when it undergoes only slight decomposition. Under considerably reduced pressure,

Glycerol, p.c.	Sp gr. at 15° compared with water at 15°	Refractive index at 15°	Glycerol, p.c.	Sp gr. at 15° compared with water at 15°	Refractive index at 15°
0	1·0000	1·3330	51	1·1318	1·4010
1	1·0024	1·3342	52	1·1346	1·4024
2	1·0048	1·3354	53	1·1374	1·4039
3	1·0072	1·3366	54	1·1402	1·4054
4	1·0096	1·3378	55	1·1430	1·4069
5	1·0120	1·3390	56	1·1458	1·4084
6	1·0144	1·3402	57	1·1486	1·4099
7	1·0168	1·3414	58	1·1514	1·4104
8	1·0192	1·3426	59	1·1542	1·4129
9	1·0216	1·3439	60	1·1570	1·4144
10	1·0240	1·3452	61	1·1599	1·4160
11	1·0265	1·3464	62	1·1628	1·4175
12	1·0290	1·3477	63	1·1657	1·4190
13	1·0315	1·3490	64	1·1686	1·4205
14	1·0340	1·3503	65	1·1715	1·4220
15	1·0365	1·3516	66	1·1743	1·4235
16	1·0390	1·3529	67	1·1771	1·4250
17	1·0415	1·3542	68	1·1799	1·4265
18	1·0440	1·3555	69	1·1827	1·4280
19	1·0465	1·3568	70	1·1855	1·4295
20	1·0490	1·3581	71	1·1882	1·4309
21	1·0516	1·3594	72	1·1909	1·4324
22	1·0542	1·3607	73	1·1936	1·4339
23	1·0568	1·3620	74	1·1963	1·4354
24	1·0594	1·3633	75	1·1990	1·4369
25	1·0620	1·3647	76	1·2017	1·4384
26	1·0646	1·3660	77	1·2044	1·4399
27	1·0672	1·3674	78	1·2071	1·4414
28	1·0698	1·3687	79	1·2098	1·4429
29	1·0724	1·3701	80	1·2125	1·4444
30	1·0750	1·3715	81	1·2152	1·4460
31	1·0777	1·3729	82	1·2179	1·4475
32	1·0804	1·3743	83	1·2206	1·4490
33	1·0831	1·3757	84	1·2233	1·4505
34	1·0858	1·3771	85	1·2260	1·4520
35	1·0885	1·3785	86	1·2287	1·4535
36	1·0912	1·3799	87	1·2314	1·4550
37	1·0939	1·3813	88	1·2341	1·4565
38	1·0966	1·3827	89	1·2368	1·4580
39	1·0993	1·3840	90	1·2395	1·4595
40	1·1020	1·3854	91	1·2421	1·4610
41	1·1047	1·3868	92	1·2447	1·4625
42	1·1074	1·3882	93	1·2473	1·4640
43	1·1101	1·3896	94	1·2499	1·4655
44	1·1128	1·3910	95	1·2525	1·4670
45	1·1155	1·3924	96	1·2550	1·4684
46	1·1182	1·3938	97	1·2575	1·4698
47	1·1209	1·3952	98	1·2600	1·4712
48	1·1236	1·3966	99	1·2625	1·4728
49	1·1263	1·3981	100	1·2650	1·4742
50	1·1290	1·3996			

Cf. Wolff (Zeitsch. angew. Chem. 1919, 32, 1).

glycerin distils unchanged. The viscosity of crude distilled glycerin is reduced during the refining process, and viscosity measurement is therefore a rapid means of determining the degree of purity (Kellner, Chem. Zentr. 1921, 92, [ii] 834).

The following table contains the most trustworthy observations made under reduced pressures (*cf. also* Richardson, Chem. Soc. Trans. 1886, 49, 746; and Kailan, Zeitsch. anal. Chem. 1912, 51, 81):—

Pressure mm.	Boiling-point °C.
385·33	260·4
347·10	257·3
231·87	250·3
201·23	241·8
100·81	220·3
50·00	210·0
45·61	201·3
30·00	191·8
20·46	183·3
12 50	179·5
10·00	167·2
6·53	161·3
5·00	155·5
0·24	118·5
0·056	115–116

Glycerol is miscible with water in all proportions. On mixing glycerol with water, a contraction of volume and an increase of temperature take place. The greatest increase of temperature, viz. 5°, is observed when 58 parts of glycerol (by weight) are mixed with 42 parts of water: the greatest contraction equals 1·1 p.c. (Gerlach). Glycerin can be completely freed from water by allowing it to stand *in vacuô* over sulphuric acid for some prolonged time.

At the ordinary temperature, glycerol does not volatilise; at the boiling-point of water, however, appreciable quantities escape with the water vapour. If glycerol be heated in an open dish on a water-bath, a slight loss is incurred, such loss depending on the shape of the vessel (whether deep or shallow), the area of the surface exposed, and the frequency with which the air over its surface is renewed.

The vapour pressure of a dilute solution of glycerol rises with the rise of temperature of the boiling solution, so that considerable amounts of glycerol volatilise with the water vapour. Theoretically, a mixture of saturated water and glycerol vapour, under the ordinary atmospheric pressure, cannot contain more than 0·2 to 0·3 p.c. of glycerol, provided that the two vapours are not miscible. Since, however, glycerol and water are miscible in every proportion, the composition of the escaping vapours cannot be calculated according to Dalton's law, but must be derived from actual observations. Gerlach determined, with the aid of a vaporimeter, in which the pressure of the vapour was measured by a column of mercury, the vapour pressures given in the table on p. 439.

Up to a concentration of about 50 p.c., no glycerol escapes with the water vapours, even if the dilute solutions be kept boiling for a prolonged time. At a concentration of about 70 p.c., traces of glycerol escape from the boiling solution (Hehner). The boiling-point of such a solution is 113·6° (*see* table). Above this concentration, noticeable amounts of glycerol escape, so that the quantitative determination of glycerol in an aqueous solution by evaporating it down on the water-bath leads to faulty results. Even if the concentration of glycerol solutions be carried out *in vacuô*, considerable proportions of glycerol escape with the water vapour when the concentration of the solution exceeds 80 p.c, (Lewkowitsch).

VAPOUR TENSIONS OF GLYCEROL AND OF AQUEOUS SOLUTIONS OF GLYCEROL (GERLACH).

Glycerol, p.c.	Water, p.c.	B.p. at 760 mm pressure, °C	Vap pressure at 100°C.
100	0	290	64
99	1	239	87
98	2	208	107
97	3	188	126
96	4	175	144
95	5	164	162
94	6	156	180
93	7	150	198
92	8	145	215
91	9	141	231
90	10	138	247
89	11	135	263
88	12	132·5	279
87	13	130·5	295
86	14	129	311
85	15	127·5	326
84	16	126	340
83	17	124·5	355
82	18	123	370
81	19	122	384
80	20	121	396
79	21	120	408
78	22	119	419
77	23	118·2	430
76	24	117·4	440
75	25	116·7	450
74	26	116	460
73	27	115·4	470
72	28	114·8	480
71	29	114·2	489
70	30	113·6	496
65	35	111·3	553
60	40	109	565
55	45	107·5	593
50	50	106	618
45	55	105	639
40	60	104	657
35	65	103·4	675
30	70	102·8	690
25	75	102·3	704
20	80	101·8	717
10	90	100·9	740
0	100	100	760

Glycerol is miscible with alcohol in all proportions. It dissolves easily in a mixture of alcohol and ether, but is sparingly soluble in ether alone, one part of glycerol, sp.gr. 1·23, requiring about 500 parts of ether. It is therefore impossible to extract glycerol from its aqueous solution by means of ether. Glycerol is soluble in acetone. Nine parts of glycerol dissolve in 100 parts of ethyl acetate. It is, however, insoluble in chloroform, light petroleum, carbon disulphide, or benzene; it is also insoluble in oils and fats (Lewkowitsch).

On heating glycerol slowly in a platinum dish to 150°–160°, it evaporates gradually without leaving a residue; at 150° it will burn with a bluish non-luminous flame without emitting any odour. If, however, glycerol is heated rapidly in a platinum dish, it burns with formation of acroleïn, and yields a residue consisting of polyglycerols.

The penetrating smell of acroleïn (which is also noticeable when glycerides are burnt, *e.g.* when an oil lamp or a tallow candle has been blown out) serves as the most characteristic reaction for the detection of the smallest quantities of glycerol. For this purpose, it is best to mix the substance under examination with dehydrating substances, such as potassium hydrogen sulphate, and heat rapidly, when acroleïn is readily formed. The most delicate reagent for detecting acroleïn in an aqueous solution is an ammoniacal solution of silver nitrate (reduction to metallic silver with production of a mirror). With Schiff's reagent, a solution of rosaniline which has been previously decolorised by sulphur dioxide, the pink colour is restored. The latter reaction, however, is less delicate than the silver test.

Glycerol has powerful solvent properties; it combines in this respect the properties of water and of ordinary alcohol; many substances dissolve even more easily in it than in either of these two latter liquids. The following table of solubilities will serve to illustrate this:—

100 parts of glycerol dissolve at 15° 98 parts of crystal soda; 60 parts of borax; 50·5 parts of potassium arsenate; 50 parts of sodium arsenate; 50 parts of zinc chloride; 48·8 parts of tannic acid; 40 parts of alum; 40 parts of zinc iodide; 40 parts of potassium iodide; 35·2 parts of zinc sulphate; 32 parts of potassium cyanide; 30 parts of copper sulphate; 25 parts of ferrous sulphate; 25 parts of potassium bromide; 20 parts of lead acetate; 20 parts of ammonium carbonate; 20 parts of arsenious acid; 20 parts of arsenic acid; 20 parts of ammonium chloride; 15 parts of oxalic acid; 11 parts of boric acid; 10 parts of barium chloride; 10 parts of copper acetate; 10 parts of benzoic acid; 8 parts of sodium bicarbonate; 7·5 parts of mercuric chloride; 5 parts of calcium sulphide; 3·7 parts of potassium chloride; 3·5 parts of potassium chlorate; 1·9 parts of iodine; about 1 part of calcium sulphate; 0·1 part of sulphur; 0·25 part of phosphorus.

An aqueous glycerol solution, of the sp.gr. 1·114, dissolves 0·957 p.c. of calcium sulphate. Metallic soaps (which are insoluble in water) are to some extent dissolved by glycerol; thus: 100 parts of glycerol, sp.gr. 1·114, dissolve 0·71 part of iron oleate, 0·94 part of magnesium oleate, and 1·18 parts of calcium oleate.

Glycerol is completely oxidised to carbon dioxide and water by potassium dichromate in an acid solution. In a dilute aqueous solution, and in the presence of caustic alkali, potassium permanganate oxidises glycerol so definitely to oxalic acid and carbonic acid (under the conditions stated below) that this reaction may be used for its quantitative determination (provided no other organic substance yielding oxalic acid be present).

Dry potassium permanganate reacts violently with concentrated glycerol. If finely powdered potassium permanganate be heaped up to form a small truncated cone and concentrated glycerol be poured into a hole made on the top, fumes escape; after a very short time the glycerol commences to froth and ignites spontaneously with violent evolution of gases.

Glycerol treated with hydrogen peroxide in presence of a ferrous salt yields glyceric aldehyde $CH_2OH{\cdot}CHOH{\cdot}CHO$.

By gentle oxidation with nitric acid, glycerol yields glyceric and oxalic acids, together with formic, glycollic, glyoxylic, and racemic acids. The glyceric acid so obtained is a racemic compound which can be resolved into optically active enantiomorphous glyceric acids (Lewkowitsch, Ber. 1883, 2720).

A strong aqueous solution of glycerol reduces Barreswil's (Fehling's) solution only slightly. On boiling the solution for 10 minutes, and allowing it to stand for 24 to 48 hours, a red or a yellow precipitate is obtained. If, however, the glycerol be diluted previously with 10 times its bulk of water, no reduction occurs.

A mixture of glycerol and silver nitrate solution heated at the temperature of boiling water with a few drops of ammonia, gives a precipitate of metallic silver. If ammonia solution be added to glycerol in the cold, and heat be then applied, as a rule no reduction takes place on adding silver nitrate, because the ammonia escapes before the glycerol has been heated sufficiently; the addition of caustic soda or potash, however, causes metallic silver to separate slowly. According to Bullnheimer, 1 part of metallic silver corresponds with 11·3 parts of glycerol.

Glycerol dissolves caustic alkalis, alkaline earths, and lead oxide, to form chemical compounds with them. The compounds so formed are termed metallic glyceroxides. Lime, strontia, and baryta are precipitated nearly completely from such solutions by carbon dioxide, a small quantity only of the earths escaping precipitation. In the presence of caustic alkalis, glycerol also dissolves ferric oxide, cupric oxide, and bismuth oxide, no doubt in consequence of the formation of soluble compounds (metallic glyceroxides), such as are represented by monosodiumcuproglyceroxide (*see* below). The oxides enumerated above are not reduced to metals, or at most only to their lower oxides. The following oxides: silver oxide (*cp.* above), gold oxide, mercury oxide, rhodium oxide, palladium oxide, and platinum oxide (Ag_2O, Au_2O_3, HgO, RhO_2, PdO, PtO_2), are reduced to metals when heated with alkaline glycerol solution (Bullnheimer).

The great solubility of zinc sulphate, as also of nickel, cobalt and copper sulphates, in glycerol, is explained by the fact that these salts combine with three molecules of glycerol to form compounds (Grün, Ber. 1908, 3465) of the general formula:

$$(M{\cdot}3C_3H_8O_3)SO_4,H_2O$$

For these compounds, the name 'glycerinates' has been proposed by Grün, in order to distinguish them from the metallic glyceroxides described above.

QUANTITATIVE DETERMINATION OF GLYCERIN.

Here only the determination of glycerol in commercial products containing considerable quantities of it can be considered. The determination of glycerol in fermented liquors falls outside the scope of this article (*see* BEER, WINE, &c.). For a description of its methods for quantitative determination, *see* Lewkowitsch, Chem. Techn. 1. For its determination in fermentation glycerin, *v.* Fleischer, Z. anal. Chem. 1921, 60, 330.

A direct method for determining glycerol in oils and fats by isolating it, has been worked out by Shukoff and Schestakoff. It is necessary to operate with a solution containing at least 40 p.c. of glycerol. If the solution be more dilute, a quantity corresponding to about 1 gram of glycerol is carefully evaporated on the water-bath, the concentration not being allowed to reach so high a degree that volatilisation of glycerol can take place (*i.e.* a concentration of about 50 p.c. must not be exceeded). Before evaporating, the solution is rendered slightly alkaline with potassium carbonate. The concentrated solution is then mixed with 20 grams of ignited and powdered anhydrous sodium sulphate and exhausted in a Soxhlet extractor with anhydrous acetone (previously well dried over ignited potassium carbonate). As acetone attacks both cork and indiarubber, all connections must be made with ground-glass fittings. The extraction requires several hours, and the results, at best, are only approximately correct.

As a rule, the determination of glycerol in oils and fats is carried out by one of the following indirect methods.

Permanganate process. The glycerol solution is made strongly alkaline and a concentrated solution of potassium permanganate is added at the ordinary temperature, until the solution is blackish. The glycerol is converted quantitatively into oxalic acid, carbon dioxide, and water, according to the following equation:

$$C_3H_8O_3+3O_2=C_2H_2O_4+CO_2+3H_2O$$

This reaction, originally suggested by Wanklyn and Fox, has been worked out as a quantitative method by Benedikt and Zsigmondy. The excess of permanganate is destroyed by adding a solution of sodium sulphite, and the oxalic acid is determined by precipitating it as calcium oxalate. It is essential that other substances which form oxalic acid on oxidation must be absent. (For a full description of the details of this method, *cf.* Lewkowitsch, Chem. Techn.) Other oxidation methods leading to the complete combustion of glycerol, can only be employed in the complete absence of organic impurities.

Acetin process. In case an impure glycerin be under examination (such as the crude glycerins described above), it is most convenient to determine the proportion of glycerol by the Benedikt-Cantor acetin process, which is based on the quantitative conversion of glycerol into triacetin on heating the solution with acetic anhydride. If the product of this reaction is then dissolved in water, and the free acetic acid carefully neutralised with alkali, the dissolved triacetin can be easily estimated by saponifying it with a known volume of standard alkali, and titrating back the excess.

Details of the method are given in the Report of the International Committee on the Analysis of Glycerin (p. 441).

Chemically pure glycerin. The proportion of glycerol in *chemically pure glycerin* is best ascertained by determining the sp.gr. (*see* table on p. 438) or by oxidising the glycerol by means of permanganate, provided organic impurities be absent. This is ascertained in the following manner: A somewhat dilute solution is mixed with a cold ammoniacal silver nitrate solution; the solution should remain colourless even after standing for 24 hours. Any acrolein present in the sample is detected by the test described above. Any polyglycerols, due to faulty distillation, are determined by allowing an accurately weighed quantity of the sample to evaporate gently at 160°. Care should be taken not to heat too rapidly, otherwise even the purest glycerol may become polymerised with the production of the very substances that are to be detected. From the weight of the residue, the weight of ash, subsequently found on incineration, must be deducted. The difference ('the organic residue') is a fair indication of the care with which the glycerol has been manufactured.

The following table gives the 'organic residue' and ash of a number of 'chemically pure glycerins' examined in the author's laboratory; they are arranged according to the amount of organic residue they contain. –

ORGANIC RESIDUE AND ASH IN COMMERCIAL CHEMICALLY PURE GLYCERINS.

(Lewkowitsch.)

No.	Residue at 160° p.c.	Ash p.c.	Organic residue p.c.
1	0·03033	0·00603	0·0243
2	0·0276	0·0030	0·0246
3	0·0377	0·0050	0·0327
4	0·0498	0·0138	0·0360
5	0·0452	0·0081	0·0371
6	0·0509	0·0066	0·0443
7	0·0656	0·0139	0·0517
8	0·0748	0·4000	0·0738
9	0·0905	0·0154	0·0751
10	0·1047	0·0190	0·0857
11	0·1236	0·0305	0·0931
12	0·1621	0·0183	0·1438
13	0·8060	0·2090	0·5970

From this table, rules for the valuation of commercial chemically pure glycerins may be derived. The first six samples certainly deserve the name of chemically pure glycerin, the following four samples represent lower qualities unfit for pharmaceutical purposes, whereas the last two samples are merely glycerins, refined by distillation; the last sample would be rejected as unsuitable even by dynamite makers. Sample No. 2 represents a chemically pure glycerin, manufactured by the author on a large scale from soap-lye glycerin, in 1890 (*cf.* Lewkowitsch, Year-Book of Pharmacy, 1890, 382; *cf.* also Thorpe, J. Soc. Chem. Ind. 1895, 720).

Chemically pure glycerin must further be free from all but the most minute traces of arsenic. This is ascertained by a modification of Gutzeit's test (*cf.* Lewkowitsch, Chem Techn.) substituting mercuric chloride for silver nitrate.

According to Kebler and Fuller (U.S. Dept. Agric. Bureau of Chem. Bull. 1912, 150), glycerin of the best quality should be neutral to litmus, leave no ash on ignition, and have sp.gr. of about 1·250 at 25°. It should not emit any odour when heated on the water-bath, or any fruity odour when warmed with alcohol and sulphuric acid. It should not contain sulphates, chlorides, oxalates, metals, or sugars, and when mixed with an equal volume of water must not reduce Barreswil's (Fehling's) solution. It should show at most a yellow coloration in Hager's test, according to which 5 c.c. of the sample are mixed with 5 c.c. of 26 p.c. ammonia solution, and 5 drops of silver nitrate solution, and left in the dark for 15 minutes at the ordinary temperature.

The British Pharmacopœia (1914) requires glycerin to have sp.gr. 1·260, to leave no appreciable ash, to be free from lead and copper, and not to contain more than 2 parts of arsenic per million.

Distilled glycerin (dynamite glycerin). The proportion of glycerol in these products is best determined by the acetin method. 'Dynamite glycerin' is usually sold according to a specification agreed upon between buyer and seller. The following conditions are usually stipulated: sp.gr. not below 1·261; absence of lime, magnesia and alumina; absence of more than traces of chlorine and of arsenic; amount of organic impurities, and total residue not to exceed a fixed quantity. In addition thereto, the 'nitration and separation' tests must be satisfactory.

Crude glycerins. All commercial transactions are now based on the following Report of the International Committee on the Analysis of Crude Glycerin (1911), the importance of which demands that it should be given in full:—

INTERNATIONAL STANDARD METHODS (1911).

'**Analysis of Crude Glycerol.** The valuation of crude glycerol has in recent years assumed greater commercial importance owing to the increased value of the commodity. The want of uniformity in the methods and processes of analysis, together with the irregularity of the results obtained, emphasised the desirability for the standardisation of crude glycerol analysis; so with this object in view committees were formed in America, France, Germany, and Great Britain. These committees worked in the first instance independently, but were ultimately brought together, and after a series of conferences the conclusions arrived at by the various committees were summarised, and drawn up in the form in which they are now presented. The methods detailed in this report have the unanimous support of each of the above committees, and are strongly recommended by them as International Standards.

'**Sampling.** The most satisfactory method available for sampling crude glycerol liable to contain suspended matter, or which is liable to deposit salt on settling, is to have the glycerol sampled by a mutually approved sampler as soon as possible after it is filled into drums, but in any case before any separation of salts has taken place. In such cases he shall sample with a sectional sampler (a suitable sampling apparatus is described in an appendix to the report), then seal the drums, brand them with a number for identification, and keep a record of the brand number. The presence of any visible salt or other suspended matter is to be noted by the sampler, and a report of same made in his certificate, together with the temperature of the glycerol. Each drum must be sampled. Glycerol which has deposited salt or other matters cannot be accurately sampled from the drums, but an approximate sample can be obtained by means of the sectional sampler, which will allow a complete vertical section of the glycerol to be taken, including any deposit.

'**Analysis.** (1) *Determination of Free Caustic Alkali.*—Weigh 20 grams of the sample into a 100 c.c. flask, dilute with approximately 50 c.c. of freshly-boiled distilled water, add an excess of neutral barium chloride solution, 1 c.c. of phenolphthalein solution, make up to the mark, and mix. Allow the precipitate to settle, draw off 50 c.c. of the clear liquid, and titrate with normal acid $\left(\frac{N}{1}\right)$. Calculate to p.c. of Na_2O existing as caustic alkali.

'(2) *Determination of Ash and Total Alkalinity.*—Weigh 2 to 5 grams of the sample in a platinum dish, burn off the glycerol over a luminous Argand burner, or other source of heat giving a low-flame temperature, the temperatures being kept low to avoid volatilisation, and the formation of sulphides. When the mass is charred to the point that water will not become coloured by soluble organic matter, lixiviate with hot distilled water, filter, wash, and ignite the residue in the platinum dish. Return the filtrate and washings to the dish, evaporate, and carefully ignite without fusion. Weigh the ash. Dissolve the ash in distilled water, and titrate total alkalinity, using as indicator methyl orange cold or litmus boiling.

'(3) *Determination of Alkali present as Carbonate.*—Take 10 grams of the sample, dilute with 50 c.c. distilled water, add sufficient $\frac{N}{1}$ acid to neutralise the total alkali found at (2), boil under a reflux condenser for 15 to 20 minutes, wash down the condenser tube with distilled water free from carbon dioxide, and titrate back with $\frac{N}{1}$ NaOH, using phenolphthalein as indicator. Calculate the p.c. of Na_2O. Deduct the Na_2O found in (1). The difference is the p.c. of Na_2O existing as carbonate.

'(4) *Alkali combined with Organic Acids.*—The sum of the p.c. of Na_2O found at (1) and (3) deducted from the p.c. found at (2) is a measure of the Na_2O or other alkali combined with organic acids.

'(5) *Determination of Acidity.*—Take 10 grams of the sample, dilute with 50 c.c. of distilled water free from carbon dioxide, and titrate with $\frac{N}{1}$ NaOH and phenolphthalein. Express in terms of Na_2O required to neutralise 100 grams.

'(6) *Determination of Total Residue at 160°.*—For this determination the crude glycerol should be slightly alkaline with Na_2CO_3, not exceeding the equivalent of 0·2 p.c. Na_2O, in order to prevent loss of organic acids. To avoid formation of polyglycerol, this alkalinity must not be exceeded.

'*Preparation of Glycerol.*—Ten grams of the sample are weighed into a 100 c.c. flask, diluted with water, and the calculated quantity of $\frac{N}{1}$ HCl or Na_2CO_3 added to give the required degree of alkalinity. The flask is filled to 100 c.c., the contents mixed, and 10 c.c. measured into a weighed Petri or similar dish 2·5 inches diameter and 0·5 inch deep, which should have a flat bottom. In the case of crude glycerols abnormally high in organic residue a less quantity is to be evaporated, so that the weight of organic residue does not materially exceed 30 to 40 milligrams.

'*Evaporation of the Glycerol.*—The dish is placed in a water-bath (the top of the 160° oven acts equally well) until most of the water has evaporated. From this point the evaporation is effected in the oven. Satisfactory results are obtained in an oven measuring 12 inches cube, having an iron plate ¼ inch thick lying on the bottom to distribute the heat. Strips of asbestos millboard are placed on a shelf halfway up the oven. On these strips the dish containing the glycerol is placed.

'If the temperature of the oven has been adjusted to 160° with the door closed, a temperature of 130° to 140° can be readily maintained with the door partially open, and the glycerol, or most of it, should be evaporated off at this temperature. When only a slight vapour is seen to come off, the dish is removed and allowed to cool.

'An addition of 0·5 to 1 c.c. of water is made, and by a rotatory motion the residue brought wholly or nearly into solution. The dish is then allowed to remain on a water-bath or top of the oven until the excess water has evaporated and the residue is in such condition that on returning to the oven at 160° it will not spit. The time taken up to this point cannot be definitely given, nor is it of importance. Usually 2 to 3 hours are required. From this point, however, the schedule of time must be strictly adhered to. The dish is allowed to remain in the oven, the temperature of which is carefully maintained at 160° for one hour, when it is removed, cooled, the residue treated with water, and the water evaporated as before. The residue is then subjected to a second baking of one hour, after which the dish is allowed to cool in a desiccator over sulphuric acid, and weighed. The treatment with water, &c., is repeated until a constant loss of 1 to 1·5 milligrams per hour is obtained.

'*Corrections to be applied to the Weight of Total Residue.*—In the case of acid glycerol, a correction must be made for the alkali added. One c.c. $\frac{N}{1}$ alkali represents an addition of 0·022 gram. In the case of alkaline crudes a correction should be made for the acid added. Deduct the increase in weight due to the conversion of the NaOH and Na_2CO_3 to NaCl. The corrected weight multiplied by 100 gives the percentage of *total residue* at 160°.

'Preserve the total residue for the determination of the non-volatile acetylisable impurities.

'(7) *Organic Residue.*—Subtract the ash from the total residue at 160°. (*Note.*—It should be noted that alkaline salts of organic acids are converted to carbonates on ignition, and that the CO_3 radicle thus derived is not included in the organic residue.)

'(8) *Moisture.*—This test is based on the fact that glycerol can be completely freed from water by allowing it to stand *in vacuô* over sulphuric acid or phosphoric anhydride. Two to three grams of very bulky asbestos freed from acid soluble material, which has previously been dried in a water-oven, are placed in a small stoppered weighing-bottle of about 15 c.c. capacity. The weighing-bottle is kept in a vacuum desiccator furnished with a supply of concentrated sulphuric acid under a pressure equivalent to 1 to 2 mm. of mercury, until constant in weight. From 1 to 1·5 gram of the sample is then carefully dropped on to the asbestos in such a way that it will be all absorbed. The weight is again taken, and the bottle replaced in the desiccator under 1 to 2 mm. pressure until constant in weight. At 15° the weight is constant in about 48 hours. At lower temperatures the test is prolonged.

'The sulphuric acid in the desiccators must be frequently renewed.

'**Acetin Process for Glycerol Determination.** This process is the one agreed upon at a Conference of Delegates from the American, British, French, and German Committees, and has been confirmed by each of the above Committees as giving results nearer to the truth on crudes in general, and is the process to be used (if applicable) whenever only one method is employed. On pure glycerols the methods are identical with those of the dichromate process. For the application of this process the crude glycerol should not contain over 50 p.c. water.

'The following reagents are required :—

'1. *Best Acetic Anhydride.*—This should be carefully selected. A good sample must not require more than 0·1 c.c. normal NaOH for saponification of the impurities when a blank is run on 7·5 c.c. Only a slight colour should develop during digestion of the blank.

'2. *Pure Fused Sodium Acetate.*—The purchased salt is again completely fused in a platinum, silica, or nickel dish, avoiding charring, powdered quickly, and kept in a stoppered bottle or a desiccator. It is most important that the sodium acetate be anhydrous.

'3. *A Solution of Sodium Hydroxide for Neutralising, of about N Strength, free from Carbonate.*—This can be readily made by dissolving pure sodium hydroxide in its own weight of water (preferably water free from carbon dioxide), and allowing to settle until clear, or filtering through an asbestos or paper filter. The clear solution is diluted with water free from carbon dioxide to the strength required.

'4. *Normal Sodium Hydroxide, free from Carbonate.*—Prepared as above, and carefully standardised.

'Some sodium hydroxide solutions show a marked diminution in strength after being boiled; such solutions should be rejected.

'5. *Normal Acid.*—Carefully standardised.

'6. *Phenolphthalein Solution.*—0·5 p.c. phenolphthalein in alcohol and neutralise.

'THE METHOD.—Into a narrow-mouthed flask (preferably round-bottomed), capacity about 120 c.c., which has been thoroughly cleaned and dried, weigh accurately and as rapidly as possible 1·25 to 1·5 grams of the glycerol. Add first about 3 grams of the anhydrous sodium acetate, then 7·5 c.c. of the acetic anhydride, and connect the flask with an upright Liebig condenser. For convenience the inner tube of this condenser should not be over 50 cm. long and 9 to 10 mm. inside.

'The flask is connected to the condenser by either a ground glass joint (preferably) or a rubber stopper. If a rubber stopper is used, it should have had a preliminary treatment with hot acetic anhydride vapour.

'Heat the contents and keep just boiling for 1 hour, taking precautions to prevent the salts drying on the sides of the flask. Allow the flask to cool somewhat, and through the condenser tube add 50 c.c. of the carbon-dioxide-free distilled water, heated to about 80°, taking care that the flask is not loosened from the condenser. The object of cooling is to avoid any sudden rush of vapours from the flask on adding water, and to avoid breaking the flask. Time is saved by adding the water before the contents of the flask solidify, but the contents may be allowed to solidify, and the test proceeded with the next day without detriment. The contents of the flask may be warmed to, but must not exceed, 80°, until the solution is complete, except a few dark flocks representing organic impurities in the crude. By giving the flask a rotatory motion solution is more quickly effected. Cool the flask and contents without loosening from condenser. When quite cold wash down the inside of the condenser tube, detach the flask, wash off stopper or ground glass connection into the flask, and filter contents of flask through an acid-washed filter into a Jena glass flask of about 1 litre capacity. Wash thoroughly with cold distilled water free from carbon dioxide. Add 2 c.c. of phenolphthalein solution (F), then run in sodium hydroxide solution (C) or (D) until a faint pinkish-yellow colour appears throughout the solution. This neutralisation must be done most carefully. The alkali should be run down the sides of the flask, the contents of which are kept rapidly swirling, with occasional agitation or change of motion, until the solution is nearly neutralised, as indicated by the slower disappearance of the colour developed locally by the alkali running into the mixture. When this point is reached the sides of the flask are washed down with carbon-dioxide-free water, and the alkali subsequently added drop by drop, mixing after each drop until the desired tint is obtained.

'Now run in from a burette 50 c.c. or a calculated excess of NaOH with $\frac{N}{1}$ acid (E) until the pinkish-yellow or chosen end-point colour just remains. A further addition of the indicator at this point will cause a return of the pinkish colour; this must be neglected, and the first end-point taken.

'From the $\frac{N}{1}$ NaOH consumed calculate the percentage of glycerol after making the correction for the blank test described below.

'1 c.c. of $\frac{N}{1}$ NaOH = 0·03069 gram of glycerol. The coefficient of expansion for normal solutions is approximately 0·00033 per c.c. for each degree C. A correction should be made on this account if necessary.

'*Blank Test.*—As the acetic anhydride and sodium acetate may contain impurities which affect the result, it is necessary to make a blank test, using the same quantities of acetic anhydride and sodium acetate as in the analysis, After neutralising the acetic acid it is not necessary to add more than 5 c.c. of the $\frac{N}{1}$ alkali (D), as that represents the excess of alkali usually left after saponification of the triacetin in the glycerol determination.

'*Determination of the Glycerol Value of the Acetysable Impurities.*—The total residue at 160° is dissolved in 1 or 2 c.c. of water, washed into a clean acetylising flask, 120 c.c. capacity. and the water evaporated Now add anhydrous sodium acetate and proceed as in the glycerol determinations before described. Calculate the result to glycerol.

'*Analysis of the Acetic Anhydride.*—Into a weighed stoppered vessel, containing 10 to 20 c.c. of water, run about 2 c.c. of the anhydride, replace stopper, and weigh; allow to stand, with occasional shaking for several hours, till all anhydride is hydrolysed; then dilute to about 200 c.c., add phenolphthalein, and titrate with $\frac{N}{1}$ NaOH. This gives the total acidity due to free acetic acid and acid formed from anhydride.

'Into a stoppered weighing-bottle containing a known weight of recently distilled aniline (from 10 to 20 c.c.) measure about 2 c.c. of the sample stopper, mix, allow to cool, and weigh. Wash contents into about 200 c.c. of cold water, and titrate acidity as before. This yields the acidity due to the original, preformed, acetic acid plus one half the acid due to anhydride (the other half having formed acetanilide); subtract the second result from the first (both calculated for 100 grams) and double result, obtaining c.c. $\frac{N}{1}$ NaOH per 100 gram sample. One c.c. NaOH equals 0·0510 gram of acetic anhydride.

'DICHROMATE PROCESS FOR GLYCEROL DETERMINATION.

'**Reagents required.** (*a*) *Pure Potassium Dichromate* powdered and dried in air free from dust or organic vapours at 110° to 120°. This is taken as the standard.

'(*b*) *Dilute Dichromate Solution.*—7·4564 grams of the above dichromate (*a*) are dissolved in distilled water and the solution made up to a litre at 15·5°.

'(*c*) *Ferrous Ammonium Sulphate.*—Dissolve 3·7282 grams of potassium dichromate (*a*) in 50 c.c. of water. Add 50 c.c. of 50 p.c. (by volume) sulphuric acid and to the cold undiluted solution add from a weighing-bottle a moderate excess of the ferrous ammonium sulphate, and titrate back with the dilute dichromate (*b*). Calculate the value of the ferrous salt in terms of dichromate.

'(*d*) *Silver Carbonate.*—This is prepared as required; for each test from 140 c.c. of 0·5 p.c. silver sulphate solution by precipitation with about 4·9 c.c. $\frac{N}{1}$ sodium carbonate solution (a little less than the calculated quantity of $\frac{N}{1}$ sodium carbonate should be used; any excess of alkali carbonate prevents rapid settling), settle, decant, and wash once by decantation.

'(*e*) *Subacetate of Lead.*—Boil a pure 10 p.c. lead acetate solution with an excess of litharge for one hour, keeping the volume constant, and filter while hot. Disregard any precipitate which subsequently forms. Preserve out of contact with carbon dioxide.

'(*f*) *Potassium Ferrocyanide.*—A very dilute solution containing about 0·1 p.c.

'THE METHOD.—Weigh 20 grams of the glycerol, dilute to 250 c.c., and take 25 c.c. Add the silver carbonate, allow to stand, with occasional agitation, for about 10 minutes, and then add a slight excess (about 5 c.c. in most cases) of the basic lead acetate (*e*), allow to stand a few minutes, dilute with distilled water to 100 c.c., and then add 0·15 c.c. to compensate for the volume of the precipitate, mix thoroughly, filter through an air-dry filter into a suitable narrow-mouthed vessel, rejecting the first 10 c.c., and return filtrate if not clear and bright. Test a portion of the filtrate with a little basic lead acetate, which should produce no further precipitate (In the great majority of cases 5 c.c. is ample.) Occasionally a crude glycerol will be found requiring more, and in this case another aliquot of 25 c.c. of the dilute glycerol should be taken and purified with 6 c.c. of the basic acetate. Care must be taken to avoid a marked excess of basic acetate. Measure off 25 c.c. of the clear filtrate into a glass flask or beaker (previously cleaned with potassium dichromate and sulphuric acid). Add 12 drops of sulphuric acid (1 : 4) to precipitate the small excess of lead as sulphate. Add 3·7282 grams of the powdered dichromate (*a*) Rinse down the dichromate with 25 c.c. of water and stand, with occasional shaking, until all the dichromate is dissolved (no reduction will take place).

'Now add 50 c.c. of 50 p.c. sulphuric acid (by volume), and immerse the vessel in boiling water for two hours, and keep protected from dust and organic vapours, such as alcohol, until the titration is completed. Add from a weighing-bottle a slight excess of the ferrous ammonium sulphate (*c*), making spot tests on a porcelain plate with the potassium ferrocyanide (*f*). Titrate back with the dilute dichromate. From the amount of dichromate reduced calculate the percentage of glycerol.

'1 gram glycerol equals 7·4564 grams dichromate.

'1 gram dichromate equals 0·13411 gram glycerol.

'*Notes.*—1. It is important that the concentration of acid in the oxidation mixture and the time of oxidation should be strictly adhered to.

'2. Before the dichromate is added to the glycerol solution it is essential that the slight excess of lead be precipitated with sulphuric acid as stipulated in the process.

'3. For "crudes" practically free from chlorides the quantity of silver carbonate may be reduced to one-fifth and the basic lead acetate to 0·5 c.c.

'4. It is sometimes advisable to add a little potassium sulphate to ensure a clear filtrate.

'**Instructions for calculating Actual Glycerol Content.**—1. Determine the apparent amount of glycerol in the sample by the acetin process as described. The result will include acetylisable impurities if any be present.

'2. Determine the total residue at 160°.

'3. Determine the acetin value of the residue at (2) in terms of glycerol.

'4. Deduct the result found at (3) from the percentage obtained at (1), and report this corrected figure as glycerol. If volatile acetylisable impurities are present, these are included in this figure.

'**Notes and Recommendations.**—Experience has shown that in crude glycerol of good commercial quality the sum of water, total residue at 160°, and corrected acetin result, comes to within 0·5 of 100. Further, in such "crudes" the dichromate result agrees with the uncorrected result to within 1 p.c.

'In the event of greater differences being found, impurities such as polyglycerols or trimethylene glycol, are present. Trimethylene glycol is more volatile than glycerol; it can therefore be concentrated by fractional distillation. An approximation to the quantity can be obtained from the spread between the acetin and dichromate results of such distillates, trimethyleneglycol showing by the former method 80·69 p.c. and by the latter 138·3 p.c. expressed as glycerol.

'In valuing crude glycerol for certain purposes it is necessary to ascertain the approximate proportion of arsenic, sulphides, sulphites, and thiosulphates. The methods for detecting and determining these impurities have not formed the subject of this investigation.

'**Recommendations by Executive Committee.**—If the non-volatile organic residue at 160° in the case of a soap lye "crude" be over 2·5 p.c. —*i.e.* when not corrected for carbon dioxide in the ash—then the residue shall be examined by the acetin method and any excess of glycerol found over 0·5 p.c. shall be deducted from the acetin figure.

'In the case of saponification, distillation, and similar glycerol the limit of organic residue which should not be passed without further examination shall be fixed at 1 p.c. In the event of the sample containing more than 1 p.c. the organic residue must be acetylated, and any glycerol found (after making the deduction of 0·5 p.c.) shall be deducted from the p.c. of glycerol found by the acetin test.'

With reference to this Report, Grimwood (J. Soc. Chem. Ind. 1913, 32, 1039) has shown that the oven recommended therein does not enable a steady temperature to be maintained. In the case of one oven he found a maximum variation of 45° between the temperatures of two shelves. In place of the standard oven he has devised an electrically heated oven cased with uralite. He also describes an accelerated method of evaporating the glycerin, in which the vapours are removed by means of an electric fan.

British Standard Specifications for Soap Lye and Saponification Crude Glycerins.—The following standard specifications were drawn up by the British Executive Committee on Crude Glycerin Analysis, and approved at a meeting of glycerin makers, buyers, and brokers held in London on October 3, 1912:—

Soap Lye Crude Glycerin.—Analysis to be made in accordance with the International Standard Methods. *Glycerol*:—The Standard shall be 80 p.c. of glycerol. Any crude glycerin tendered which test 81 p.c. of glycerol or over, shall be paid for at a *pro rata* increase, calculated as from the standard of 80 p.c. Any crude glycerin which tests under 80 p.c. of glycerol, but is 78 p.c. or over shall be subject to a reduction of 1½ times the shortage, calculated at the *pro rata* price as from 80 p.c. If the test falls below 78 p.c. the buyer shall have the right of rejection. *Ash.*—The standard shall be 10 p.c. In the event of the percentage of ash exceeding 10 p.c., but not exceeding 10·5 p.c., a percentage reduction shall be made for the excess calculated as from 10 p.c. at *pro rata* price, and if the percentage of ash exceeds 10·5 p.c., but does not exceed 11 p.c., an additional percentage reduction shall be made equal to double the amount in excess of 10·5 p.c. If the amount exceeds 11 p.c. the buyer shall have the right to reject the parcel.

Organic Residue.—The standard shall be 3 p.c. A percentage deduction shall be made of three times the amount in excess of the standard of 3 p.c., calculated at *pro rata* price. The buyer shall have the right to reject any parcel which tests over 3·75 p.c.

Saponification Crude Glycerin.—Analysis to be made in accordance with the International Standard Methods. *Glycerol.*—The standard shall be 88 p.c. Any crude glycerin which tests 89 p.c. or over shall be paid for at a *pro rata* increase calculated as from the standard of 88 p.c. Any crude glycerin which tests under 88 p.c., but is 86 p.c. or over, shall be subject to a reduction of 1½ times the shortage, calculated at *pro rata* price as from 88 p.c. If the test falls below 86 p.c., the buyer shall have the right of rejection. *Ash.*—The standard shall be 0·5 p.c. In the event of the percentage of ash exceeding 0·5 p.c., but not exceeding 2·0 p.c., a percentage reduction shall be made equal to double the amount in excess of 0·5 p.c. If the amount of ash exceeds 0·2 p.c. the buyer shall have the right to reject the parcel.

Organic Residues.—The standard shall be 1 p.c. A percentage deduction shall be made of twice the amount in excess of the standard of 1 p.c., calculated at *pro rata* price. The buyer shall have the right to reject any parcel which tests over 2 p.c.

Estimation of Trimethylene Glycol.—The proportion of trimethylene glycol in crude glycerin may be approximately estimated by distillation under reduced pressure and determining the sp.gr. and apparent glycerol content (by the acetin method) of the distillate (Salway, J. Soc. Chem. Ind. 1918, 37, 123T). From these data the amount of trimethylene glycol may be calculated by means of the following formula, assuming only glycerol, water, and trimethylene glycol to be present:—

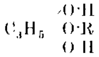
$$\text{Sp.gr.} = 1 + 0{\cdot}00263x + 0{\cdot}00053y$$
$$\text{Apparent glycerol content} = x + 0{\cdot}81y$$

If the amount of trimethylene glycol is less than 1 p.c., it is necessary to fractionate the glycerol, and apply the tests to the fraction boiling at 110°–280°.

ESTERS OF GLYCEROL.

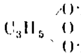
The most important esters of glycerol are those resulting from the combination of one molecule of glycerol with three molecules of fatty acids. These esters occur in largest quantities in the natural oils and fats which represent a mixture of a number of simple and mixed triglycerides (*see* OILS, FIXED, AND FATS).

Glycerol, being a trihydric alcohol, is able to form mono-acid and di-acid esters, which are usually described as monoglycerides and diglycerides (although these terms must be considered incorrect, for the term 'monoglyceride' should more appropriately be applied to a triglyceride containing one and the same acid radicle, and the term 'diglyceride' to a triglyceride containing two different acid radicles) The *monoglycerides* have the general formula:



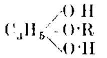
$$C_3H_5\begin{matrix}O\cdot H\\ O\cdot R\\ O\cdot H\end{matrix}$$

According to the position which the fatty acid radicle occupies in the molecule, two isomeric glycerides may exist, as is explained by the following two formulæ, in which R denotes the fatty acid radicle:—



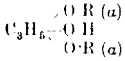
$$C_3H_5\begin{matrix}O\cdot R\\ O\cdot H\\ O\cdot H\end{matrix}$$

or

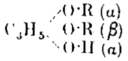


$$C_3H_5\begin{matrix}O\cdot H\\ O\cdot R\\ O\cdot H\end{matrix}$$

Compounds of this composition contain an asymmetric carbon atom, and may therefore represent racemic compounds. Monoglycerides corresponding to the first formula are termed **α**-monoglycerides, and those corresponding to the second formula are termed β monoglycerides. If a second acid radicle enters, the so-called diglycerides are obtained. Theoretically, two isomeric diglycerides containing the same fatty acid radicle are possible, as is indicated by the following two formulæ:—



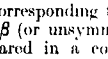
$$C_3H_5\begin{matrix}O\cdot R\ (\alpha)\\ O\cdot H\\ O\cdot R\ (\alpha)\end{matrix}$$



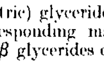
$$C_3H_5\begin{matrix}O\cdot R\ (\alpha)\\ O\cdot R\ (\beta)\\ O\cdot H\ (\alpha)\end{matrix}$$

The compounds conforming to the first formula are denoted **αα** (or symmetric) glycerides; they are prepared from αα-dichlorohydrin and the salts of fatty acids. The compounds corresponding to the latter formula are termed **αβ** (or unsymmetric) glycerides; they are prepared in a corresponding manner from β-dibromohydrin. $\alpha\beta$ glycerides contain an asymmetric carbon atom; hence the synthetically prepared $\alpha\beta$ diglycerides are likely to represent racemic compounds. If one or both of the acid radicles were optically active (*e.g.* if derived from ricinoleic, chaulmoogric, or hydnocarpic acid), the diglycerides would be optically active on that account alone.

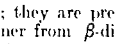
If the two fatty acid radicles are different, the existence of diglycerides having the following formulæ is theoretically possible:—



$$C_3H_5\begin{matrix}O\cdot R_1\\ O\cdot H\\ O\cdot R_2\end{matrix}$$



$$C_3H_5\begin{matrix}O\cdot R_1\\ O\cdot R_2\\ O\cdot H\end{matrix}$$



$$C_3H_5\begin{matrix}O\cdot R_2\\ O\cdot R_1\\ O\cdot H\end{matrix}$$

These diglycerides may be termed 'mixed diglycerides.' As they all contain an asymmetric carbon atom they may represent racemic compounds. If one or both acid radicles be derived from optically active fatty acids, the diglycerides containing them will exhibit optical activity.

The monoglycerides and diglycerides do not occur in nature, but very strong evidence has been adduced that these esters are formed in the course of slow hydrolysis of the natural triglycerides; hence they may be found in fats and oils which have become rancid by a natural process on exposure to air, light, and moisture.

Glycerol also forms esters with inorganic acids, such as sulphuric, nitric, phosphoric, boric, and arsenious acids.

A mixed triglyceride, containing two acid radicles of fatty acids and one of phosphoric acid, occurs in nature as *Lecithin*, in which two fatty acid radicles and one acid radicle of phosphoric acid are combined with the glycerol rest. In the phosphoric acid radicle, one of the two free OH groups is combined with the base choline. Lecithin appears to be a representative of a whole group of mixed triglycerides (occurring in the liver, in the brain, &c.), which have been termed by Thudichum, phosphatides, and more recently by Leathes, phospholipines.

Mixed triglycerides containing, in addition to one or two fatty acid radicles, two or one radicles of inorganic acids other than phosphoric acid have not been met with in nature; they have, however, been prepared synthetically. Representatives of such mixed glycerides are chlorodilaurin, chlorodimyristin, chlorodistearin, and monostearochlorohydrin.

The sulphuric acid esters of glycerol are obtained by dissolving glycerol in concentrated sulphuric acid. On boiling with steam, the esters are easily dissociated into glycerol and sulphuric acid. All three possible glycerol sulphuric acids, glyceroltrisulphuric acid, glyceroldisulphuric acid, and glycerolmonosulphuric acid are known.

Glycerylphosphoric esters are obtained by heating phosphoric acid with glycerol. The most important ester, commercially, is monoglycerolphosphoric acid, which forms a series of salts (sodium, lithium, calcium, strontium, iron, &c.), largely used in pharmaceutical practice (especially in France).

It has been found by Umney and Bennett (Proc. Brit. Pharm. Conf. 1914, 22) that the composition of commercial calcium glycerophosphate varies. It should contain at least 15 p.c. of calcium, and may contain added citric acid to increase the solubility. The magnesium salt should contain not less than 10 p.c. of magnesium, and the ferric salt at least 15 p.c. of iron, and be soluble in 2 parts of water. Sodium glycerophosphate crystallises with 5 molecules of water.

For a method of examining glycerylphosphoric esters, *see* Grimbert and Bailly (Compt. rend. 1915, 160, 207; Bailly, *idem.* 1915, 161, 677).

Optically active glycerophosphoric acid may be synthesised by adding phosphorylchloride to a solution of *d*-α-bromohydrin in dry pyridine at below −10°. The bromine is removed by lithium hydroxide and the product is isolated as nearly pure lithium *d*-glycerophosphate $HO\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot O\cdot PO(OLi)[\alpha]_D^{18}=+3\cdot 51°$

in aqueous solution. Lithium *l*-glycerophosphate has $[a]_D^{18°} = -3·02°$ (Abderhalden and Eichwald, Ber. 1918, 51, 1308).

Of great commercial importance are the nitric esters of which the most important is glyceryl trinitrate, or 'nitroglycerin,' prepared by allowing glycerin to run into a mixture of one part of strongest nitric acid and two parts (by weight) of concentrated sulphuric acid. Nitroglycerin is a heavy oily liquid of sp.gr. 1·60, which volatilises at 160° under a pressure of 15 mm. Its most remarkable property of exploding violently under certain conditions is made use of in high explosives and 'smokeless powders,' such as 'dynamite,' 'blasting gelatin,' 'gelignite,' &c. (*v.* EXPLOSIVES).

The mono- and dinitrates of glycerol and their chlorides and ethers are employed as ingredients of non-freezing nitroglycerin blasting combinations. The dinitrate of monochlorohydrin is used in such explosives as gelatin astralit, gelatin westfalit, &c. The nature and explosive character of α-methylin dinitrate (glyceryl methyl ether dinitrate) have been investigated by Trevor Jones (Chem. Soc. Trans. 1919, 76) (*v.* EXPLOSIVES).

Glyceryl arsenite is formed by dissolving arsenious oxide in glycerol and heating to 250°. Above 250° it decomposes. It is volatile with the vapours of glycerol, hence, when distilling glycerin in a current of superheated steam (*see* above), the arsenite is either volatilised unchanged, or is hydrolysed by the steam; at any rate the distillate contains arsenious acid. Glyceryl arsenite is used in calico printing.

POLYGLYCEROLS.

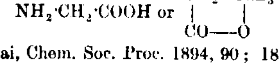
When glycerol is heated rapidly, polyglycerols are obtained. They are formed by the combination of several molecules of glycerol with loss of water: hence they are formed on a large scale during the distillation of glycerin, when the bulk of the polyglycerols remains behind in the still. The condensation of glycerol to polyglycerol has been effected by Lourenço, by heating glycerol with monochlorohydrin. (For the application of polyglycerols in the arts, *see* above.) J. L.

GLYCERIN-FORMAL. A condensation product of glycerol and formaldehyde.

GLYCEROLPHOSPHORIC ACID and **GLYCEROLPHOSPHATES** *v.* GLYCERIN (GLYCEROL).

GLYCIN is the trade name for the chloride of *p*-hydroxyphenylaminoacetic acid. It is used in photography as a developer (also *v.* GLYCINE).

GLYCINE. *Glycin, Glycocine, Glycocoll, Aminoacetic acid*



$$NH_2·CH_2·COOH \text{ or } \begin{array}{l} CH_2—NH_3 \\ | \quad\quad\;\; | \\ CO——O \end{array}$$

(Sakurai, Chem. Soc. Proc. 1894, 90; 1896, 38; Walker, Chem. Soc. Proc. 1894, 94). Glycine was discovered in 1820 by Braconnot (Ann. Chim. [2] 13, 114) among the products obtained by decomposing glue with sulphuric acid. It is obtained by decomposing various protein substances with sulphuric acid (Spiro, Zeitsch. physiol. Chem. 28, 187), and is present as the chief amino-acid in the sugar cane (Shorey, J. Amer. Chem. Soc. 1897, 881; 1898, 137). It may be prepared by treating bromacetic or chloracetic acids with ammonia (Perkin and Duppa, Annalen, 108, 112; Kraut, Ber. 1890, 2577; Mauthner and Suida, Monatsh. 11, 374; Goldberg, Kunz and Kraut, Annalen, 266, 295); by treating chloracetic acid with ammonium carbonate (Nencki, Ber. 1883, 2828); by passing cyanogen into boiling hydriodic acid (sp.gr. 1·96) (Emmerling, Ber. 1873, 1361); by heating potassium phthalimide with ethyl chloracetate (Gabriel and Kroseberg, *ibid.* 1889, 427); by treating nitrosomalonic ester with zinc and acetic acid (Conrad and Schulze, *ibid.* 1909, 729); by boiling hippuric acid with strong sulphuric acid (Curtius, J. pr. Chem. [2] 26, 145; Dessaignes, Annalen, 58, 322); by treating glyoxylic acid with ammonium carbonate and subsequently heating to 120° with hydrochloric acid (Erlenmeyer, junr., and Kunlin, Ber. 1902, 2438); by the action of hexamethylene amine on potassium monochloracetate (Bourcet, Bull. Soc. chim. 19, [3] 1005; Auger, *ibid.* 21, [3] 5). In order to obtain the pure acid, the solution containing the acid, prepared by any of the above methods, is freed from ammonia (if present) and freshly precipitated copper hydroxide is added. The copper salt of the acid crystallises out; this is filtered off and decomposed with sulphuretted hydrogen. Another method consists in extracting the acid with glycerol and thus separating it from the impurities present (Farbw. Meister, Lucius and Bruning, D. R. P. 141976; Zeitsch. angew. Chem. 1903, 16, 527). Siegfried (D. R. P. 188005; Chem. Zentr. 1907, ii. 1466) adds barium or strontium hydroxides to the solution, passes in carbon dioxide, filters off the separated solid and heats it with water.

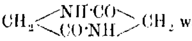
Properties.—Glycine crystallises from water in plates and from dilute alcohol in needles. After drying at 100° the plate form begins to decompose on heating at 212°, whilst the needle form remains unchanged until a temperature of 220° to 230° is reached, when they melt with the evolution of gas at 232°–236°; sp.gr. 1·1607 (Curtius, *l.c.*). It is soluble in 4·3 parts of cold water and in 930 parts of ethyl alcohol (sp.gr. 0·828), but is insoluble in absolute alcohol. Hydriodic acid reduces glycine to ammonia and acetic acid (Kwisda, Monatsh. 12, 419), whilst sodium amalgam yields amino-acetaldehyde (Neuberg, Ber. 1908, 956; Fischer, *ibid.* 1019). On electrolysis, the acid or the copper salt yields ethylenediamine (Lilienfeld, D. R. P. 147943; Chem. Zentr. 1904, i. 133; Kühling, Ber. 1905, 1638; 1907, 757). Hydrogen peroxide oxidises glycine to glyoxylic acid and formaldehyde (Dakin, J. Biol. Chem. 1, 171); treatment with nitrosyl chloride results in the formation of chloracetic acid (Tilden and Forster, Chem. Soc. Trans. 1895, 491). Glycine and its derivatives are used in photography as developers, in place of pyrogallol, &c. (Farbw. Meister, Lucius and Bruning, D. R. P. 142489; U.S. Pat. 767815; Eng. Pat. 20377; J. Soc. Chem. Ind. 1903, 380), and also for reducing silver images.

Derivatives.—*Aromatic glycines* are prepared from aromatic amines and monohalogenated acetic acids or dihalogenated vinyl ethers (Imbert and Consortium fur Elektrochemische Industrie, Chem. Soc. Abstr. 1908, i. 975;

D. R. P. 190624). *Glycocollamide* is produced when glycocoll and alcoholic ammonia are heated together at 160°. *Glycocollanilide* is prepared from chloro- or bromo- acetanilide and ammonia (Majort, Eng. Pat. 5269; D. R. P. 59121; J. Soc. Chem. Ind. 1892, 369). The *Ethyl ester* is prepared by the action of ammonia on chloracetic acid, and subsequent treatment of the crude dry product with absolute alcohol and dry hydrogen chloride (Hantzsch and Metcalf, Ber. 1896, 1684; Hantzsch and Silberrad, *ibid.* 1900, 70) or by the interaction of hexamethylene amine and chloracetic acid and subsequent treatment as above (Auger, Bull. Soc. chim. [3] 21, 5). It boils at 51·5°–52·5° (10 mm), and has sp.gr. 1·0358 11·8°/4° (Schmidt, Ber. 1905, 200).

Methylglycine v. SARCOSINE.

Trimethylglycine v. BETAINE.

Glycine anhydride  $CH_2<\genfrac{}{}{0pt}{}{NH\cdot CO}{CO\cdot NH}>CH_2$ was discovered by Curtius (J. pr. Chem [2] 37, 173). It separates out from an aqueous solution of glycine ester on long standing. It is best prepared by treating the hydrochloride of the ester with caustic soda (Fischer, Ber. 1906, 2893). It is a white crystalline solid, which, on heating, becomes brown at 245° and melts at 275°.

Glycocollaminocarboxylic acid esters (*v.* Einhorn, Chem. Zentr. 1901, i. 1115; D. R. P. 108027).

GLYCOBROM. Syn. for the glyceryl ester of dibromohydrocinnamic acid.

GLYCOCHOLEIC ACID *v.* CHOLIC ACID.

GLYCOCOLL *v.* GLYCINE.

GLYCOCYAMINE. Syn. for guandine acetic acid.

GLYCOGEN *v.* CARBOHYDRATES.

GLYCOL. *See* Ethylene Glycol, art. ETHYL.

GLYCOLLIC ACID. *Hydroxyacetic acid*

$CH_2(OH)COOH$

juice present as the chief acid constituent in the Chem. Soc. 189 sugar cane (Shorey, J. Amer. calcium precipitat. i. 45) and is found in the beet-juice (Lippmann, rmed in the treatment of formed by the oxidat Ber. 1891, 3299). It is Annalen, 103, 366); by t. of glycol (Würtz. nitric acid in the cold (Dr ting alcohol with 150); by reducing oxalic acid hsel, *ibid.* 127, crand, Bull. Soc. chim. [ii.] 39, ith zinc (Forelectrolytic reduction of oxalic aci); by the hydrochloric or sulphuric acids, usin dilute electrodes (Roessler and Hasslacher Che g lead U.S. Pat. 837083; D. R. PP. 194038, 204. Co., J. Soc. Chem. Ind. 1907, 157; 1909, 107; Rainhold, Fr. Pat. 378276; J. Soc. Chem. Ind. 1907, 1097; Avery and Dales, Ber. 1899, 2236); and by treating formaldehyde with equivalent quantities of potassium cyanide and calcium chloride (Kohn, Monatsh. 1899, 903; Franzen, J. pr. Chem. [2], 1912, 133). Glycollic acid may be prepared by boiling a concentrated solution of potassium chloracetate for 24–30 hours in a flask under a reflux apparatus. The product is then distilled under reduced pressure, the temperature being kept below 70°. The residue is mixed with a large quantity of acetone, the solution filtered from the separated potassium chloride, and after a short time the glycollic acid separates from the acetone solution in colourless crystals. The yield is about 85 p.c (Colman, Chem. Soc. Proc. 1892, 72; *cf.* Witzemann, J. Amer. Chem. Soc. 1917, 39, 109).

Glycollic acid crystallises from water in crystals belonging to the monoclinic system and from acetone in those of the orthorhombic system (Colman, *l.c.*); m.p. 78·9° (Drechsel, *l.c.*). On heating to 100°, glycollic anhydride $C_4H_6O_5$ is formed, and by heating the calcium salt with much sulphuric acid, metaformaldehyde is produced. Oxidation with nitric acid yields oxalic acid, and reduction with zinc and sulphuric acid results in the formation of acetic acid (Claus, Annalen, 145, 256). It may be detected by heating 0·02–0·1 gram of the substance with 0·2 c.c. of water and 2 c.c. of sulphuric acid (sp.gr. 1·84); after gas has ceased to be evolved, the addition of one drop of *p*-cresol gives a green coloration, or one drop of codeine solution, a yellow coloration changing to deep violet (Denigès, Bull. Soc. chim. 1909, 5, 647).

The glycollates of the alkalis are deliquescent; calcium glycollate $(C_2H_3O_3)_2Ca$ (with 3 or $4\frac{1}{2}$ H_2O) and silver glycollate $C_2H_3O_3Ag,\frac{1}{2}H_2O$ are sparingly soluble in water.

The ammonium salt may be distilled *in vacuô*, the distillate consisting of the acid ammonium glycollate, boiling at 160° under 10 mm. pressure (D. R. P. 247240).

GLYCOSAL. Trade name for a combination of glycerol and salicylic acid introduced as a substitute for other salicylates (*v.* SYNTHETIC DRUGS).

GLYCURONIC ACID

$CHO\cdot HCOH\cdot OHCH\cdot HCOH\cdot HCOH\cdot COOH$

occurs in urine in combination with phenol, kresol, and indoxyl. It is also present in the blood. It does not occur in the free state, but is produced in the body in considerable quantity after the administration of certain substances, *e.g.* camphor, menthol, phenol, &c., in combination with which it is eliminated. It thus appears to furnish a material which can be produced by the body to neutralise the toxic properties of harmful substances before their elimination. It occurs also in combination in plants. It is found in combination with euxanthone in the urine of camels: the Mg salt of the euxanthone-glycuronic acid is the basis of the pigment Indian yellow. It may be synthesised by reducing saccharic acid with sodium amalgam in acid solution (Fischer and Piloty, Ber. 1891, 521).

Preparation.—It is prepared from its compounds by boiling with acid: thus, menthol-glycuronic acid is split by boiling with dilute sulphuric acid; camphor glycuronic acid is ariled with hydrochloric acid for 2 hours; prec saturating the solution with $PbCO_3$ the *Pro* ated lead salt is decomposed with H_2S. readily *rties.*—Glycuronic acid is a syrup, lactone, ning water in a vacuum, forming a Tollens, Ann ting from 170°–175° (Mann and +19·25°. It en, 290, 155). Rotation $[\alpha]_D^{18°}$ = reduced to g is oxidised to saccharic, and it breaks up uconic, acid. Distilled with HCl, which may binto furfurol and CO_2, a reaction fermented by y used for its estimation. Not reducing substeast. It is said to be one of the the sugars hanges left in urine from which fermentation. ve been removed by yeast.

Detection and Estimation.—With a solution of orcin in hydrochloric acid it gives a green colour after boiling for a short time. With naphthoresorcin and HCl it gives a blue substance soluble in ether, showing a well-marked absorption band in the neighbourhood of the D line and differentiated by its solubility in ether from the substances given under similar circumstances by the pentoses (Tollens, Ber. 1908, 1788). This reaction is, however, given by other acids (Mandel and Neuberg, Biochem. Zeitsch. 13, 148). It gives a characteristic *p*-bromphenylhydrazone, melting at 236°. The phenylosazone is formed on heating a mixture of 1 molecule glycuronic acid with 3 molecules phenyl hydrazine in acetic solution to 40° for some days. It melts at 200°–205°. The semicarbazone melts at 188°.

GLYCYPHYLLIN *v.* Glucosides.

GLYCYRRHETIN, GLYCYRRHIZIC ACID, GLYCYRRHIZIN *v.* Liquorice.

GLYOXYLIC ACID $CHO\,CO_2H$ or

$$CH(OH)_2CO_2H$$

Found in very young beet-roots (Lippmann, Ber. 1891, 3305), in grapes, unripe apples, plums, gooseberries, currants, and rhubarb (Brunner and Chaud, Ber. 1886, 595; Bull. Soc. chim. [3] 13, 126). Prepared by oxidising alcohol (Debus, Annalen, 100, 1; Boettinger, Arch. Pharm. 232, 65), glycol (Debus, Annalen, 110, 316) or glycerol (Heintz, *ibid.* 152, 325) with nitric acid; by heating ethyldichloracetate with water at 120° (Fischer and Geuther, J. 1864, 316); by exactly neutralising dichloracetic acid with potassium hydroxide (1 : 1) and heating with solid potassium acetate in a reflux apparatus for an hour, filtering the liquid and boiling the filtrate for several hours (Doebner, Annalen, 311, 129); by heating the silver salt of dibrom- or dichloracetic acid with water (Debus, Zeitsch. Chem. 1866, 188; Perkin and Duppa, Annalen, 112, 24; Zeitsch. Chem. 1868, 424; Beckurts and Otto, Ber. 1881, 581); by heating one part of dibromacetic acid with 10 parts of water for 24 hours at 135°-140° (Grimaux, Bull. Soc. chim. [ii.] 26, 483); by reducing the esters of oxalic acid with sodium amalgam (Bayer & Co. D. R. P. 201895; J. Soc. Chem. Ind. 1908, 1176); by the electrolytic reduction of oxalic acid, its esters or its amide in sulphuric acid at a low temperature (Tafel and Friedrichs, Ber. 1904, 3187; Wohl and Lange, *ibid.* 1908, 3614; Kinzlberger & Co. D. R. PP. 163842, 210693; J. Soc. Chem. Ind. 1906, 392; 1909, 815).

Glyoxylic acid is a thick liquid, readily soluble in water, and crystallises in rhombic prisms by long standing over sulphuric acid (Debus, Chem. Soc. Trans. 1904, 1382); the crystals have the formula $C_2H_4O_4$ (Perkin, Ber. 1875, 188). It is a tautomeric substance; it exhibits aldehydic properties in condensing with hydroxylamine, phenylhydrazine, and semicarbazide (Elbers, Annalen, 227, 353; Fischer, Ber. 1884, 576; Simon and Chavanne, Compt. rend. 143, 904), but most of its salts are of the type $(HO)_2CH{\cdot}CO_2M$, whilst dialkyl ethers of the type $(RO)_2{\cdot}CH{\cdot}CO_2H$ have been prepared. Reduction with zinc in aqueous solution yields glycollic acid; in acetic solution, tartaric acid (Genvresse, Compt. rend. 114, 555): nitric acid oxidises it to oxalic acid, whilst potash simultaneously oxidises and reduces it with the formation of glycollic and oxalic acids: treatment with ammonia and subsequent hydrolysis yields formic acid and glycine (Erlenmeyer and Kunlin, Ber. 1902, 2438). With hydrogen cyanide, it forms a cyanhydrin which, on hydrolysis, yields tartronic acid. By warming with resorcinol and a little absolute alcohol, diluting and adding a few drops of ammonia, a deep blue coloration is produced, rapidly changing to red (Boettinger, Arch. Pharm. 232, 1); sulphuric acid gives a blue or violet coloration with glyoxylic acid (Hopkins and Cole, Proc. Roy. Soc. 68, 21). The phenylhydrazone melts at 137°, and is used for identifying the acid. It condenses with carbamide to form allantoin and with guanidine to form in the cold glyoxylic guanidide and on warming to 100°, iminoallantoin (Doebner and Gärtner, Annalen, 315, 1; 317, 157; Simon and Chavanne, Compt. rend. 143, 51; Kaess and Gruszkiewicz, Ber. 1902, 3604). For other condensations *v.* Boettinger, Arch. Pharm. 232, 549, 704; 233, 100, 199; Bougault, Compt. rend. 148, 1270. For salts *v.* Debus, Chem. Soc. Trans. 1904, 1382. Glyoxylic acid acts as a hydrolysing agent towards cane sugar and starch, and prevents fermentation of products thus formed as it acts on yeast as a poison (Boettinger, Arch. Pharm. 233, 287; Bouveault, Bull. Soc. chim. [iii.] 19, 78). For physiological action in the body, *v.* Eppinger, Beitr. chem. Physiol. Path. 6, 492; Almagia, *ibid.* 7, 459; Schloss, *ibid.* 8, 445; Granstörm, *ibid.* 11, 132; Dakin, J. Biol. Chem. 1, 271; Hofbauer, Zeitsch. physiol. Chem. 52, 425; Adler, Arch. exp. Path. Pharm. 46, 207.

GMELINOL $C_{12}H_{14}O_4$, the white deposit in the cells of the 'Colonial Beech' (*Gmelina Leichhardtii* F. *v.* M.), separating from hot water in needle prisms or plates. M.p. in the crystalline state 122° (corr.). After cooling solidifies to a transparent, resin-like substance which melts at 62°–63°. When powdered the m.p. begins to rise, soon reaches 120°–121°, $[\alpha]_D$+ 123·3° in chloroform. Soluble in 1470 parts of water at 22°. Nitric acid converts it into a *dinitro-* compound $C_{12}H_{12}O_4(NO_2)_2$, m.p. 128°–129°. Sodium acetate and acetic anhydride transform it into a *monoacetyl* derivative, m.p. 110°. With bromine water forms

$$C_{12}H_{13}O_4Br$$

Zeisel determinations indicate the presence of two methoxy-groups, and this is confirmed by the production of veratric acid when the substance is oxidised by a solution of chromic acid in glacial acetic acid, or by alkaline permanganate. When fused with potassium hydroxide at a temperature not exceeding 200°, phenolic substances are formed, whilst at 210°–225°, protocatechuic acid is produced, together with small quantities of a volatile acid (H. G. Smith, J. Roy. Sci, New S. Wales, 1913, 46, 187).

GNEISS *v.* Granite.

GNOSCOPINE *v.* Opium.

GOA POWDER *v.* Chrysarobin.

GOETHITE or **GÖTHITE.** Hydrated ferric oxide, $Fe_2O_3{\cdot}H_2O$ or $FeO(OH)$, crystallised in the orthorhombic system and isomorphous with the corresponding aluminium and manganese minerals diaspore and manganite. It is included with limonite under the term '*brown iron-ore*,' and when fibrous and massive the two are not readily distinguished, especially as they have the same colour and streak. Goethite, however, contains more iron (Fe_2O_3 89·9, Fe 62·9 p.c.) and less water (10·1 p.c.) than limonite ($2Fe_2O_3 \cdot 3H_2O$). Crystals of goethite are not uncommon; limonite, on the other hand, though sometimes fibrous and crystalline, is never crystallised. They are prismatic, acicular, platy, or scaly in habit, and have a perfect cleavage in one direction (parallel to the brachy-pinacoid). Reniform and stalactitic masses with a radiating fibrous structure also occur. Sp gr. 4·0–4·4, of crystals 4·37; H. 5–5½. The colour is yellowish-brown to brownish-black, with usually a brilliant lustre on crystal-faces. Thin crystals and splinters are blood-red by transmitted light. The colour of the streak or powder is yellowish-brown. Analyses often show the presence of small amounts of manganese oxide and silica. Several varieties are distinguished. The acicular forms, usually with a radial grouping, are known as *needle iron-ore*. The needles may be very fine and closely packed together, giving the appearance of plush, as in *Sammetblende* or *Sammeterz* (velvet-ore), also known as *przibramite*, from Przibram in Bohemia. Another form occurring as extremely thin scales with a reddish colour is known as *Rubinglimmer* or *Pyrrhosiderite*; and a scaly-fibrous or plumose form as *lepidocrocite*. *Onegite* is acicular goethite embedded in amethyst from Lake Onega, Russia. This material is cut as a gem-stone under the name 'Cupid's darts' (flèches d'amour). As an enclosure in other gem-minerals it is represented in avanturine and sun-stone. *Mesabite* is an ochreous variety abundant amongst the iron ores of the Mesabi Range in the Lake Superior district of Minnesota. The name goethite is after the poet Goethe. The modes of occurrence of goethite are the same as for limonite, and it is present in many limonitic iron ores. Fine groups of crystals were formerly obtained in abundance in the Restormel iron mines at Lanlivery and in the Botallack mine at St. Just in Cornwall. Larger, but less perfect, crystals are known from the Pike's Peak district in Colorado. L. J. S.

GOLD. Sym Au (Aurum). At.wt. 197·2.

Historical.—Gold cannot have escaped the observation of the men of the Stone Age, but it could have been of little use to them except for ornamentation until they had discovered the art of melting. Flint daggers with gilt handles have been found in Egypt, and gold was well known in that country about 3600 B.C., when its value in relation to silver was fixed by law. It was first used for coinage in Lydia, about 700 B.C. in the form of electrum, a native alloy of gold and silver.

The earliest method of obtaining gold, other than that of collecting it by hand, was by washing with water on sloping rocks. Sheep-skins were spread out for entangling the particles of metal and helping in its collection. Over 2000 years ago, the methods of ore-crushing by hammers and also by means of pestles and mortars were adopted in Egypt to release gold contained in solid rock. The powdered ore was washed on sloping tables. The use of sieves is also attributed to the Egyptians. Heavy pestles or stampers, requiring water power or the united efforts of several men to raise them, were not employed until much later. Stamp batteries for crushing ore were established at Joachimsthal in 1519, and sieves set at the outlet of the mortars were described by Agricola in 1556 and were seen by Jars in the Hartz in 1767.

The use of mercury for separating gold from other materials by amalgamation was described by Pliny and referred to by Theophilus in the 11th century in his description of the extraction of gold from the sands of the Rhine. The method used in the Tyrol of stirring crushed ore with large quantities of mercury in circular bowls is of great antiquity, but the practice of charging mercury together with uncrushed ore into the mortars of stamp batteries and catching the gold amalgam on copper plates was not mentioned before 1850.

The chlorination process of gold ore treatment originated in 1848, and the cyanide process was invented by MacArthur and Forrest in 1887. The methods of refining gold by the cementation process and by cupellation are very ancient. Nitric acid for refining was in use in Venice in the 15th century and was not superseded by sulphuric acid until the 19th century. The electrolytic refining process, invented in 1888, has now replaced the sulphuric acid process in the United States.

Gold ores. Gold is widely distributed in nature. It occurs in minute traces in all ores of silver, copper, lead, antimony, and bismuth. It has been detected in igneous and metamorphic rocks in almost every case in which a careful search for it has been made, and sedimentary rocks are seldom quite free from it. The comparatively small quantities of gold in limestones which have been formed in clear water far from land, appear to indicate the land as the place of origin of the gold, but it is also present in sea water.

Gold occurs in quantities large enough to pay for extraction in many quartz veins or lodes in rock formations. The gold is disseminated in the quartz and is accompanied by brown oxides of iron in the upper portions of the deposits and by sulphides in the deep-seated portions. It usually occurs as native gold and even when it is contained in pyrites or other sulphides, it is present in the free state. Native gold also occurs in many secondary or detrital ('placer') deposits, such as river gravels, sea beaches, &c., in the form of nuggets, grains, and flakes. The auriferous beds of conglomerate in the Transvaal are of this character.

Native gold occurs in the form of rounded, irregularly shaped nuggets, pellets, grains, &c., which show crystalline structure when polished and etched but rarely exhibit regular crystal faces or angles externally. It always contains some silver and copper, and other metals are also generally present in smaller proportions.

Telluride of gold is found in large quantities in Western Australia, Colorado, and Transylvania, and has been reported from many other localities. There is only one true compound of gold and tellurium, which corresponds with the formula $AuTe_2$, and contains 43·6 p.c. of gold; but several compounds consisting of various mixtures of tellurium with gold and silver and other metals have been recognised as mineral species. The best known of these are (1) *calaverite*, which has the composition $AuTe_2$, (2) *sylvanite* or graphic tellurium which appears to be a variable mixture of $AuTe_2$ and Ag_3Te_4, (3) *petzite*, a telluride of silver, Ag_2Te, with part of the silver replaced by gold, and (4) *nagyagite* or foliated tellurium, which contains some lead.

Auriferous telluride is usually dark grey or black in colour, but occasionally is silver-grey. Sometimes it contains an admixture of metallic gold which gives it a brassy-yellow colour. It is soft and brittle but its density is high, usually between 8 and 9. When heated in air, it oxidises, fuming and giving off TeO_2, and fuses below a red heat. If the roasting process is continued, most of the tellurium is removed and the gold is left in the form of spherical pellets which have solidified from fusion. Calaverite may contain as much as 44 p.c. of gold, but part of this is usually replaced by silver. A specimen of sylvanite from Cripple Creek, Colorado, contained gold 7·64 p.c., silver 32·39 p.c., tellurium 59·96 p.c. (F. C. Smith), and a specimen of petzite from California contained 25·6 p.c. of gold and 41·86 p.c. of silver.

Extraction of gold from its ores. The metallurgical treatment of gold ores is usually simple and cheap and owing to this circumstance and to the high value of the metal, ores containing very small proportions of gold can be worked at a profit. Thus the ores of the Witwatersrand, now being worked, contain, on an average, only about 6 or 7 dwt. of gold per ton, or little more than 0·001 p.c., and in the case of auriferous gravel a ton rarely contains more than a few grains of gold.

Washing auriferous gravel.—The gold occurring in placers is obtained by washing away, with the aid of water, the lighter gravel from the gold disseminated through it. A large number of appliances and machines are in use for this purpose. Generally the larger stones are removed by some form of sieve and the finer material is carried by a shallow stream of water through inclined troughs ('sluice-boxes') or over sloping tables. The heavy particles of gold sink to the bottom of the stream and are caught by the rough surface of blanketing or plush or in crevices which are formed by the supply of 'riffles' of various kinds. Sometimes the riffles consist of wooden strips or poles, sometimes of iron rails or sheets of 'expanded' metal. Mercury is sprinkled in the stream and accumulates in the crevices, where it assists in catching the gold by amalgamating with it. The gold-amalgam, recovered in the periodical 'clean-up,' is strained through canvas to remove the excess of mercury and afterwards retorted.

The gravel is mined in various ways, according to circumstances. It may be raised by the spade and thrown into the stream, or when in high banks it may be broken down and washed away by jets of water ('hydraulic mining'). Gravels cemented by infiltration are crushed before being washed. Of late years, dredgers have been largely used, originally to recover the gravel from river beds and more recently on dry alluvial 'flats.' In the latter case, the dredger floats in a pond, and travels slowly across country, scooping away the ground in front and stacking it behind after it has been washed. Placer mining is now of less relative importance than formerly owing to the exhaustion of many of the known deposits.

Stamp battery.—Auriferous quartz is usually treated by crushing in stamp batteries and amalgamation. The residue or tailing is subsequently treated in various ways, especially by the cyanide process. In recent years, especially in the United States, the use of mercury has been discarded in many cases in favour of the cyanide process, and the use of other crushing machines instead of stamps is also increasing.

Stamps are heavy iron or steel pestles which are lifted and let fall in iron mortars. They have gradually increased in weight, the 50 lb. stamps of 100 years ago having become the 900 lb. stamps of the nineties and the 1800 or 2000 lb. stamps which have been installed in the Transvaal. The height of drop is usually about 7 or 8 inches and the number of drops per minute about 100. Water and ore are fed into the mortar continually and the fall of the stamps splashes the mixture against a wire screen or perforated metal plate set in the side of the mortar. The finely comminuted material passes through the screen and usually falls directly upon gently sloping amalgamated copper plates. Sometimes mercury is fed into the battery with the ore and amalgamated plates are fastened to the inside of the mortar, but these practices are becoming less common and are impossible with modern heavy stamps. It is now considered advantageous to remove the amalgamated plates to another building at some distance from the stamp battery in order to avoid excessive vibration. Stamps are usually in batteries of five, working side by side in a single mortar, but the Nissen stamp has a separate mortar for each stamp and has other distinctive features.

The pulp from the battery is often further reduced in size by passing through a tube-mill, a revolving cylinder half-filled with pebbles, and in that case a coarser mesh is used in the battery screens. No screens are used in tube-mills. Amalgamated plates are placed at the outlets of the tube-mills, and those between the battery and the tube-mills are sometimes omitted. Other machines are occasionally used for fine grinding, as, for example, amalgamating pans (*see* article Silver for description of these machines). Roller mills, such as the Huntington mill, are sometimes used instead of stamps for crushing soft or brittle ores, or as intermediate grinders. In the Huntington mill, four rollers with vertical axes run around in an iron pan, and are pressed against its periphery by centrifugal force.

In some of the most modern gold extraction works in the Transvaal, the ore is broken to a maximum size of about 1¾ inch in rock-breakers of the reciprocating type in which the jaws alternately advance and recede. Gyratory rock crushers are also used. The ore is then passed to the stamp battery and crushed by heavy stamps through coarse screens up to ½ inch aperture, the maximum dimensions of ore which can be advantageously treated in tube-mills. Under these conditions, the amount of ore crushed per stamp per day is as much as 20 tons against 4 or 5 tons in adjoining mills where lighter stamps and finer sieves are used. Such coarse material as that indicated above cannot be passed over amalgamated plates, as these would be scoured free from mercury, &c., and it is accordingly passed direct to (inverted) cone classifiers, where the coarse particles settle in water and are retained, whilst the fine material is carried away in the overflow, and sent to the cyanide works. A diaphragm guards the axis of the cone so that the settlement of the sands takes place round the periphery. The underflow or discharge from the apex of the cone, containing the coarse material, including all the coarse free gold, is fed into tube-mills together with some of the water from the overflow. On issuing from the tube-mill, the pulp, which now contains only a small proportion of material too coarse to pass through a 60-mesh sieve (aperture 0·008 inch), is slightly diluted with water and then passed over amalgamated plates where the coarse free gold is extracted. The tailing from the plates is discharged into the stream of pulp coming from the battery and again passes to the cone classifiers, the oversize being thus returned to the tube-mill. The material passing through the tube-mill contains much less water (say 2 parts of water to 1 of ore) than that coming from the battery and that going to the cyanide works. The last-named pulp is in a very finely divided state and contains no coarse free gold. It is thus in a suitable condition for treatment by cyanide.

Classifiers other than simple cones are also in use in various parts of the world, such as the Dorr classifier in North America, and their work is assisted in some mills by concentrators such as Wilfley tables. The sulphide obtained by concentration is usually rich in gold and is treated either by cyaniding or by smelting with lead ore. Formerly such material was, in many cases, ground with mercury in pans, or treated by chlorination, but these methods have been discarded.

Amalgamation depends on the property possessed by mercury of 'wetting' gold when brought in contact with it. In battery amalgamation, the crushed pulp flows in a thin stream over sloping tables covered with sheet copper, the surface of which has been amalgamated by rubbing with mercury. Particles of gold, silver, or amalgam, on coming in contact with the amalgamated surface adhere to it and so the plate becomes covered with amalgam of the precious metals. In order to increase the chances of contact between the gold and the plates, little falls or steps down of 2 or 3 inches in height are sometimes made between the upper and lower parts of the inclined tables. It has been found that the catching powers of the plate improve as amalgam of the precious metals accumulate on it, and it is accordingly usual to electroplate the copper with silver before amalgamating it or to dress it with silver-amalgam or even with gold-amalgam. The surface is kept bright and untarnished by cleaning with cyanide, and additional mercury is sprinkled on if the amalgam-surface becomes hard and dry from the accumulation of silver and gold. The excess of amalgam is brushed off at intervals and squeezed in canvas bags to separate the surplus mercury. The pasty amalgam retained by the canvas is then retorted and the residue melted with suitable fluxes and cast into bars.

Gold will absorb about six times its weight of mercury, forming a silver-white solid amalgam containing about 13·5 p.c. of gold, but in ore treatment, time does not admit of the complete saturation of the gold with mercury, which slowly penetrates into the solid metal by diffusion. The result is that the gold-amalgam collected in cleaning-up in a gold mill consists of little 'nuggets' of gold immersed in a bath of mercury by which their outside layers are saturated. When the mixture is strained through canvas, the excess mercury passes through carrying some gold in solution and leaving behind most of the gold with its adherent mercury. If the gold is very finely divided, the penetration by mercury is more nearly complete, and the percentage of gold in the solid amalgam smaller than if the particles of gold are comparatively large. The composition of the amalgam is also affected by the extent to which other metals are present, as these also form solid amalgams with mercury and reduce the value of the product. Generally speaking, squeezed amalgam resulting from the treatment of gold ores contains from 20 to 50 p.c. of gold. It may also contain silver, copper, iron, &c., in varying proportions.

One of the difficulties in amalgamation is the 'flouring' or 'sickening' of mercury, due chiefly to the presence of arsenic or certain other impurities in the ores. The mercury is broken up into a number of excessively minute globules which have the appearance of flour, and is then swept away in the stream of ore and water and lost in the tailing. Impure mercury containing lead, zinc, &c., is easily floured, as the base metals oxidise and form a coating over the surface of the globules of mercury, thus preventing them from coalescing. The remedy is to purify the foul mercury by distillation, but in the treatment of certain ores it soon again becomes impure. The violent action of stamps on mercury when it is fed into the mortars also causes its excessive subdivision, and it is now unusual to feed mercury into the mortars, the practice being in any case permissible only with light stamps.

Another difficulty is caused by the discoloration of the copper plates, which become covered by a film of oxide or carbonate, with the result that their catching powers are impaired. The attack on the plates is generally caused by acidity of the water due to oxidation of iron sulphide, &c., in the ore. Sometimes the difficulty has been met by the addition of caustic lime to the ore in order to keep the pulp neutral or alkaline. Stains on the plates are removed by brushing with a solution of potassium cyanide. Plates which have been coated with electrodeposited silver are more easily kept in good condition than others.

The treatment of ore by passing it over amalgamated plates removes only a part of the gold, the percentage varying with the ore. In many cases from 50 to 70 p.c. of the gold can be recovered in this way, very few ores being completely 'free-milling,' *i.e.* yielding all their gold to mercury. Some ores are highly 'refractory,' yielding little when subjected to amalgamation, and these are treated by cyaniding or by smelting. Concentration by flotation has also been applied successfully to gold ores and previous amalgamation is then unnecessary in some cases. The tailing is usually worth treatment by cyanide.

The cyanide process.—The tailing from amalgamation contains some finely divided gold which escapes extraction by mercury but is usually readily soluble in solutions of the cyanides of the alkali metals. The solvent action of cyanide on gold is very slow and requires the presence of an oxidising agent such as free oxygen. It may be expressed by the following equation, which represents the sum of the chemical actions:—

$$4Au+8KCN+O_2+2H_2O=4KAu(CN)_2+4KOH$$

The potassium aurocyanide formed in this way remains dissolved in the water. The oxygen required is dissolved in the cyanide solutions from the air in contact with it. If the oxygen is exhausted owing, for example, to the cyanide solutions remaining for some time in contact with ore containing readily oxidisable sulphide or organic matter, dissolution of the gold is stopped, and it is necessary to aerate the pulp. Very dilute solutions of cyanide are used, containing from about 0·5 p.c. to as little as 0·001 p.c. of potassium cyanide.

Crushed ore or tailing is treated in large vats (containing as much as 400 tons of ore) with false bottoms provided with filter beds. Cyanide solution is run on to the ore and allowed to percolate through it. Fresh solution is added from time to time and finally the ore is washed with water. The solutions pass through the filter by which they are clarified and are conveyed to the precipitation boxes, where the gold is separated, as described later.

Some ores are not amalgamated before treatment with cyanide. In these cases, it may be advantageous to crush in cyanide solution instead of water, and the method is used at the Black Hills, Dakota, and in many other mills in America. At first the ore was crushed in stamp mills as already described, but other forms of crushers have passed into use in the last few years. Among these may be mentioned: (*a*) the Hardinge mill, a conical or pear-shaped mill half-filled with steel balls, working on the principle of the tube-mill; (*b*) the Marcy mill, a short tube-mill containing steel balls, or rods, working without screens; (*c*) Chilian mills, which resemble mortar mills, the crushing being effected by edge-runners rolling round a circular iron pan; (*d*) pairs of rolls between which the ore passes.

There are numerous modifications in the cyanide process necessitated by the conditions or introduced as improvements. Of these, the variations in mechanical treatment are the most important and complex. Difficulties in leaching crushed ore are caused by the presence of 'slime' or impalpable particles which render the ore impervious to the passage of liquids, unless it is treated in thin layers. To avoid this difficulty, the crushed ore is divided into sand and slime in 'classifiers,' by taking advantage of the difference in the rate of settlement of the particles in water. The 'sand' consists of the particles which settle readily in water. It is easily leached, liquids passing through it under the action of gravity with great rapidity. It is sometimes separated from the excess of water contained in it ('de-watered or 'thickened') by means of filters, and is treated by simple leaching as indicated above. The 'slime' does not readily settle in water, and cannot be leached directly except under high pressure.

The classification may be effected by merely running the stream of pulp into a large vat filled with water, when the sand settles and fills the vat and the slime is carried off in the overflow. Either the sand is cyanided where it settles or it is drained and transferred to another vat for the purpose, thus becoming well mixed and aerated. Another method of separation is by the use of 'spitzlutten' or pointed troughs, in which a rising current of water carries off the slime, the heavy sand falling through the water and being discharged at the apex of the trough. Cone classifiers and other modern appliances have already been mentioned in connection with tube-mills. Various devices are in use for the even distribution of the sand in filling the treatment vats.

The treatment of slime is becoming the most important part of the cyanide process. In 'all-sliming' methods, the sand is reground until it can be included with the slime, so that no separate treatment is required. In many cases the gold is not completely laid open to attack until the ore is ground to slime and the recognition of this fact has led to a wide adoption of the all-sliming policy. The slime is treated by agitation, especially in Pachuca tanks, in which a column of pulp mixed with air rises in a large pipe placed in the tank, and overflows at the top. The gold is dissolved and the ore separated from the cyanide solution by (1) decantation, (2) filtration, or (3) counter-current decantation.

(1) In the decantation process, the slime is thickened by settlement and decantation, often with the aid of dissolved lime (by which the slime is coagulated), and is then agitated with dilute cyanide solutions and washed by decantation in conical vats. Slime is usually aërated by the passage of compressed air which is forced through perforated pipes at the bottom of the vats, thus serving to agitate the pulp at the same time. The addition of about 0·25 p.c. of oxides of manganese and iron to the slimed pulp, and the use of air-agitation on the same charge (Adair-Usher process) has been widely adopted in the Transvaal.

(2) In slime filtration, the thickened pulp is agitated with cyanide solution and filtered with the aid of a vacuum (as in the Oliver, Moore, Ridgway, and Butter's filter presses), or by direct pressure (as in the Merrill, Burt, and other filter presses). Even a thin layer of slimed ore offers great resistance to the passage of liquids, and an enormous area of filtering surface is required for operations on a large scale. This is obtained by using a number of parallel filter plates or leaves placed near together. A vacuum is formed in the narrow space between two leaves and the liquid filters into it. The slimed ore gradually forms a cake on the filter surface and is washed with clear water in that position. After being washed, the cakes of

slime are detached by blowing air through in the reverse direction or by other methods.

(3) Counter-current decantation. This is a continuous process, the slimed ore settling through a rising current of solution (or wash-water) and being withdrawn at the bottom of the vat for transference to the top of the next vat. The solution enters at the bottom of the vat and overflows at the top, so that it moves in the reverse direction to the ore through the series of vats.

The gold contained in pyrites or other sulphide is less readily soluble than ordinary free gold, owing to the absorption of oxygen by the sulphide. When the sulphide is separated as concentrate by the use of travelling-belt vanners, Wilfley tables, or other machines, this disadvantage becomes serious, and such material, as has been mentioned above, is sometimes shipped to smelting works instead of being treated by cyanidation.

Ores may also contain 'cyanicides' by which potassium cyanide is destroyed as such. Acidity of the ore due to oxidation of sulphide is not uncommon and this is corrected by washing with alkali before the cyanide solution is applied, or by crushing the ore with lime. Certain cupriferous ores destroy so much cyanide that they cannot be treated profitably by the process.

The treatment of telluride ore by cyanide presents great difficulties, as potassium cyanide acts very slowly on telluride of gold. Either the ore must be roasted in order to expel the tellurium before cyaniding, or an addition of bromocyanogen must be made to ordinary KCN. The mixture readily dissolves telluride of gold. If coarse free gold is present in the telluride ore, it is extracted by amalgamation. In Western Australia, the telluride ores, after treatment in various ways, which involve roasting the concentrate or the whole of the ore, regrinding in tube-mills, classification, agitation with cyanide, &c., are almost universally filter-pressed.

Precipitation of gold from cyanide solutions may be effected by zinc shavings contained in long boxes divided into compartments by means of partitions which force the solution to flow through the zinc upwards and downwards alternately. The zinc is coated with lead by immersing the shavings in a solution of lead acetate, in order to expedite the precipitation, especially in weak solutions. The zinc dissolves in the cyanide solution and gradually wastes away. The gold is precipitated chiefly in the form of black slime. Oxygen in the solution delays precipitation and may even reverse the action. This difficulty is overcome by the Crowe or vacuum process of de-aerifying cyanide solutions preparatory to precipitation (Morg. and Sci. Press, Aug. 23, 1919, p. 257). In 'cleaning up,' the zinc is washed free from cyanide and digested in sulphuric acid or sodium disulphate, until all action has ceased. The residue now freed from zinc is washed, filtered, dried, and fused in pots with borax, manganese dioxide, or nitre, and sodium carbonate. After casting, the bullion is separated from the slag and sold to refineries. An alternative method is to smelt the gold-zinc slime with litharge, charcoal, &c., and to cupel the base lead-bullion produced (Tavener process. In modern practice, precipitation is often effected with zinc-dust which is agitated with the clear cyanide solution. The precipitated gold is separated by filter pressure and is smelted at once without previous acid treatment. Another method of precipitation is by means of finely ground charcoal, which is subsequently burnt, leaving the gold in the ashes. The effective agent is supposed to be carbon monoxide contained in the charcoal (Edmands, Bull. Inst. Mng. and Met. Feb. 1918).

Smelting.—Gold ores containing appreciable quantities of lead or copper are usually smelted for the production of these metals, from which the gold is subsequently extracted. Other gold ores are sometimes useful as fluxes in the smelting operations (*see* articles COPPER and LEAD).

Refining. Gold extracted from ores is usually impure and unfit for use in the arts until it has been refined. Preliminary refining or 'toughening' operations are often carried out either at the refineries or at the gold mills before the bullion is sold. Sometimes the gold is melted in crucibles with oxidising agents such as nitre, or a blast of air is directed on the surface of the molten metal or even passed through it. The base metals are oxidised and form a dross which is skimmed off with the help of bone ash, or borax is added to form a fusible slag with the oxides of the metals. In the Transvaal, the gold precipitate obtained in the cyanide process is often refined by cupellation with excess of lead (Tavener process). Toughened bullion contains little except gold, silver, and copper.

In London and on the Continent of Europe, gold bullion is usually refined by 'parting' with sulphuric acid. In this process, an alloy of gold and silver is prepared by melting gold bullion with 'doré' silver (*i.e.* silver containing small quantities of gold) or Mexican dollars or occasionally with refined silver if no other is available. The parting alloy usually contains from 20 to 30 p.c. of gold and a few p.c. of copper. If a higher proportion of gold is present, some silver remains undissolved and is retained by the gold. The copper assists the dissolution of the silver.

The alloy is granulated by being poured into water while still molten and the granulations are boiled in concentrated sulphuric acid of sp.gr. 1·85 in cast iron kettles. The amount of acid used is four or five times the weight of the granulations, but only about half this amount is added at first. The sulphur dioxide, which is formed in large quantities, is carried away through leaden pipes. Silver sulphate is retained in solution in the hot concentrated acid, but tends to be precipitated when the acid is cooled or diluted. When the evolution of sulphur dioxide is at an end, the liquid is transferred to a settling pot, and fresh acid added. After three boilings in acid, the 'brown gold' residue is washed with boiling water, dried, melted with nitre, and cast into ingots of about 400 ozs. each in open moulds.

The acid solution of silver is poured into large lead-lined tanks containing hot water and sheet or scrap copper, and is heated by means of steam and stirred until the precipitation of the silver is complete. The silver precipitate is washed, dried, and compressed into cakes by hydraulic power before being melted. The solution is alternately concentrated by evaporation and allowed to cool, successive crops of crystals of copper sulphate being obtained, of which the first is the purest. As an alternative the copper is removed from its solution by electrolysis. The gold produced by sulphuric acid parting is usually from 996 to 999 fine, and the precipitated silver is about 996 or 998 fine. Formerly nitric acid was used at Philadelphia as an adjunct to the sulphuric acid process before the introduction of the electrolytic process.

In the United States, in Canada, and in some refineries in London and Germany, gold is refined by electrolysis. Two processes are used successively. In the *Moebius process*, a parting alloy containing not more than 30 p.c. of gold and at least 70 p.c. of silver, copper, lead, &c., is electrolysed in a solution containing about 2 p.c. of free nitric acid and 3 p.c. of silver in the form of nitrate. Silver, copper, and some other metals are dissolved at the anodes, and silver is deposited at the cathodes which consist of rolled sheets of pure silver. The current density is 7·5 amperes per square foot of cathode surface at Philadelphia, and as much as 20 amperes per square foot at Denver. The silver is deposited in a coherent form on the cathodes with the help of a little gelatin in the electrolyte and is subsequently stripped off. The gold remains undissolved at the anodes and retains some silver. The copper, lead, zinc, &c., accumulate in the electrolyte, which is kept in condition by the addition of silver nitrate and by frequent renewal. The gold anodes are sometimes boiled in sulphuric acid, but if they contain as much as 950 parts of gold per 1000, they may be melted at once and cast into anodes for treatment by the Wohlwill process.

In the *Wohlwill process*, the anodes contain not more than 50 parts of silver per 1000 and a few parts per 1000 of base metals. By the use of a 'pulsating' current (a combination of a direct and an alternating current), it is claimed that material containing a greater proportion of silver can be treated, as the silver chloride is automatically detached from the anodes. The electrolyte contains from 2 to 10 p.c. of hydrochloric acid and from 2·5 to 6 p.c. of chloride of gold. It is heated to a temperature of 60° to 70°. The higher strengths are in use at Denver, where a high current density of 60 amperes per square foot is used. If the hydrochloric acid is insufficient in amount, or if the electrolyte is not hot enough, or if too high a current density is used, some chlorine is given off at the anodes and a corresponding amount of gold remains undissolved. The anodes are made of such thickness (4 to 12 mm.) that they can be dissolved in from 24 to 36 hours under the conditions of treatment. The cathodes consist of fine gold and the deposit on them is almost pure gold, so that copper, lead, zinc, tellurium, &c., accumulate in the solution, to which it is necessary to add gold chloride at frequent intervals. The residue at the anodes consists chiefly of silver chloride, but any platinum that may be present remains there and some gold is also left undissolved. The anode mud is boiled in sulphuric acid which converts the AgCl into Ag_2SO_4.

The gold and silver refined by electrolysis are of high quality. They can easily be made over 999 fine and are always free from lead and other deleterious elements which are occasionally left in small quantities in the gold refined by sulphuric acid, rendering it unfit for use in the arts.

Chlorine process. In Australia and Canada, gold is refined by the passage of a stream of chlorine gas through the molten metal, a method invented by Miller in 1867. The chlorine is conveyed through a clay pipe, which is inserted in the metal. Zinc, iron, &c., are chloridised first and are sometimes removed by a current of oxygen before chlorine is passed through. Silver is attacked last, and the end of the operation is recognised by the appearance of a characteristic 'flame,' denoting that the chlorine, which in the earlier stages is completely absorbed, has begun to pass unchanged through the metal. The fused chlorides are baled out into moulds and the refined gold stirred and cast into ingots. The chlorides, which contain from 5 to 10 p.c. of gold, are remelted and small quantities of sodium bicarbonate are added without stirring. Some silver is reduced at the surface of the charge, and falling through the chlorides carries down the gold with it. An alloy is thus produced, containing from 40 to 60 p.c. of gold, which is again passed through the refining process. The slabs of silver chloride are boiled in water to free them from the chlorides of copper, zinc, &c., and the silver is then reduced by means of iron and hydrochloric acid. The refined gold is about 996 fine. The method is inconvenient if a large proportion of silver is present in the bullion to be refined.

Properties of gold. The characteristic yellow colour of gold is made redder by the presence of copper and paler by the presence of silver. In certain proportions the effect of one of the two metals neutralises that of the other. Molten gold is green in colour, and very finely divided gold is usually of some shade of purple, as in the case of gold which has been volatilised and condensed.

Gold is the most extensible of all metals, and can be reduced by hammering to a thickness of 0·00008 mm. Its malleability and ductility are reduced by the presence of impurities, of which bismuth, lead, and tellurium have the most striking effects. Gold containing 0·25 per 1000 of bismuth is brittle. The melting-point of pure gold is 1064°, but if 0·2 p.c. of tellurium is contained in it, it softens at 432°, the melting-point of the eutectic of gold and the compound $AuTe_2$. The presence of most other metals reduces the melting-point of gold, but platinum raises it and silver does not materially affect it, unless it amounts to at least 30 p.c. of the alloy. The density of cast gold is about 19·3, but that of precipitated gold is higher, varying up to 20·72.

Gold is unaffected by the air at all temperatures and can be melted and solidified without being changed. In large pieces, it is not perceptibly attacked by alkalis or by nitric, sulphuric, or hydrochloric acid, but, when finely divided, it is slightly soluble in boiling HCl and in boiling HNO_3. It is freely soluble in *aqua regia* or other mixtures, evolving one of the halogens, and more slowly by cyanide solutions in the presence of air. Its compounds are generally formed with difficulty and decomposed very easily with the isolation of the metal.

Alloys of gold. The *gold-copper* alloys are harder, more fusible, of higher tensile strength, and less malleable and ductile than pure gold. The metals are miscible in all proportions when molten and on solidification separate only to a slight degree. The first additions of copper to gold cause a rapid lowering of the melting-point, the minimum of 884° being reached at the alloy containing gold 82 p.c., copper 18 p.c. This alloy is somewhat brittle, breaking under the hammer with a conchoidal fracture, and is unsuitable for the manufacture of wares. The densities of the alloys when cast are as follows:—

Proportion of gold	Density
100 p.c.	19·30
91·66 ,,	17·35
90·0 ,,	17·17
75·0 ,,	14·74
58·3 ,,	12·69
25·0 ,,	10·03

When the alloys are rolled or hammered, the densities are higher, and the densities of gold wares, which consist of triple alloys of gold, silver, and copper, are also higher.

Gold-silver alloys are soft, malleable, and ductile and all their properties are intermediate between those of gold and silver. The colour is dominated by the silver, the alloy containing 37·5 p.c. of gold being only just distinguishable in colour from pure silver. Alloys containing not less than 65 p.c. of silver are almost completely parted by boiling nitric or sulphuric acid, the silver being dissolved and the gold left behind as a brown sponge or powder. The gold obstinately retains about 0·1 p.c. of silver, and on continued boiling in strong nitric acid, some gold is dissolved whilst the proportion of silver is reduced very slowly. The presence of copper facilitates the action of the acid but does not alter the final result.

Amalgams or alloys of gold and mercury are formed at ordinary temperatures by direct union of the two metals. Mercury dissolves 0·11 p.c. of gold at 0° and 0·126 p.c. at 100°, and gold absorbs about 6 times its weight of mercury, forming a silver-white solid alloy containing about 13·5 p.c. of gold. At 440° most of the mercury is removed by volatilisation, the residue containing about 75 p.c. of gold. At a bright red heat, almost all the remainder of the mercury is distilled off. In the alternative, the mercury can be removed by dissolving it in nitric acid. Parravano (Gazz. chim. ital. 1918, 48, ii. 123) states that gold amalgams contain at least two compounds Au_2Hg_3 and Au_3Hg (*cf.* Paal and Steyer, Kolloid Zeitsch. 1918, 23, 145).

Gold-iron alloys are hard but malleable and ductile. Alloys, containing between 15 and 20 p.c. of iron, are used in jewellery in France under the name *or gris*. Their colour is greyish-yellow and they melt at temperatures higher than that of pure gold. *Or bleu* contains 25 p.c. of iron. It melts at a temperature of 1160°.

Gold forms a brittle purple compound with aluminium, containing 21·5 p.c. of aluminium and having the formula $AuAl_2$ assigned to it. The compound AuZn, containing 25 p.c. of zinc, is of a pale lilac colour and is also brittle. There are many other intermetallic compounds containing gold, usually brittle substances of a silver-white or greyish colour. Zinc removes gold from molten lead, forming the compound $AuZn_8$, and aluminium has the same property, the compound formed being $AuAl_2$.

Uses of gold. Gold is used in the form of its alloys with copper, silver, &c., in the manufacture of coin, plate, and jewellery. Gold leaf is used for gilding by hand and potassium aurocyanide is used in gold plating baths. Gold is also used in photography (in the form of sodium chloro-aurate); in dentistry (as alloys); in medicine (as the chloride); and in the manufacture of mirrors for reflecting purposes. In the form of purple of Cassius, and as leaf it is used for colouring glasses, glazes, and enamels. The aid of a flux is employed in its application in glazing and a mixture of the composition 30 parts precipitated gold, 15 of black mercurous oxide, 2·5 of basic bismuth nitrate, and 0·3 of melted borax is recommended. The addition of 3 parts of silver carbonate produces a greenish tint. After firing the gold has a matt surface and must be polished with bloodstone or agate. A cheaper process, which does not require polishing after firing, is in the use of 'Glanz gold' or 'Meissen gold,' a preparation of gold solution with an organic medium such as turpentine, lavender oil, and a balsam or resin. Gold lace consists of excessively fine strips of gold twined round silk and contains about 2·5 p.c. of gold by weight.

Manufacture of coin.—The standards of fineness of 916·6 (British Empire, Turkey, and Portugal), and 900 (most other countries) are used generally for current coin, the exception being Egypt where the standard is 875. The alloy is principally copper, but small quantities of silver are present in most coins, the proportion being higher in old ones. Fine gold was used for coinage for a time in Ancient Greece and also in Rome, under the Republic, but copper was afterwards added to reduce the cost. Fine gold is still used for some medals. It is now universally admitted that the alloy with copper is better than pure gold for coinage, owing to its lower melting-point, which is advantageous in the manufacture, and its greater hardness, which enables it to resist defacement better and perhaps to be less readily abraded. The only disadvantages of the alloy with copper are that it blackens when heated and is made brittle by the presence of a minute proportion of lead or tellurium. Fine gold is not affected until the proportion of lead is five or six times as high (0·15 p.c. as against 0·025 p.c.).

In the manufacture of coin, refined gold is melted with copper in graphite crucibles and cast into bars in upright (closed) iron moulds. Charges of about 2500 ozs. are used at the Royal Mint and the fuel is ordinary illuminating gas with a blast of air. Naphtha gas or oil are in use at some other mints, but solid fuel has now been discarded generally. The loss of gold in melting is about 0·2 per 1000, about half of which is volatilised and can be recovered by the use of suitable condensing chambers. The remainder is in the 'mint sweep.'

After being assayed, the gold bars are rolled down, blanks or discs are cut out by punches, and the blanks annealed in gas furnaces, air being excluded. The blank is placed in a collar and struck between dies by means of a lever press. A single blow suffices for the production of each coin, the design on each side being impressed simultaneously, while the metal is forced laterally by the pressure into the corrugations of the collar. Finally, the coins are weighed singly on automatic balances which reject those outside the limits of weight allowed by law.

Gold wares.—The alloys used in the manufacture of gold wares consist of gold, silver, and copper. The wares are usually made from rolled plates which are cut out by punches and struck between dies. The pieces are fitted together by hand, usually by means of soldering. Solders generally contain less gold than the parts which have to be joined together. Decorative work is carried out by hand-hammering, engraving, chasing, &c. The wares are 'coloured' or pickled by a process which removes the silver and copper from the surface and leaves a coating of pure gold, afterwards burnished. In pickling, the wares are heated to redness in air and the blackened surface is removed by boiling in dilute sulphuric or nitric acid, after which the colour is improved by immersion in hot mixtures of nitre, common salt, alum, &c. The standards of gold wares authorised by law in the United Kingdom are 22-carat (*i.e.* containing 22 parts of gold out of 24) 18-, 15-, 12-, and 9-carat. Other standards are in use abroad.

Imitation gold wares sometimes consist of alloys of copper with aluminium, zinc, &c., and sometimes of a thin plate of gold laid on a bar of base metal and rolled out for use in manufacture. Electro-plating is carried out in baths containing potassium aurocyanide with anodes of pure gold. The bath is used hot and the anode is of about the same dimensions as the article to be gilded. Gold chloride is added to the bath, as required, to keep it at the strength of about one ounce of gold to the gallon (6·85 g. of gold per litre). In Japanese art, alloys of copper containing a small proportion of gold are used to enable a beautiful purple patina to be produced on the surface. The alloys are known as *Shakudo* and *Shibuichi*.

Gold leaf contains from 90 to 98 p.c. of gold, the rest being silver and copper. The metal is cast into little flat bars which are rolled out with frequent annealings until about 0·33 mm. thick. The strip of gold is then cut into pieces of 1 inch square and these are interleaved with vellum and beaten with a 16-lb. hammer to 4 inches square. They are again cut up and beaten out between gold-beaters' skins. The book of 25 leaves, each about 3¼ inches (8·25 cm.) square, contains from 4 to 10 grains (0·26 to 0·65 gram) of gold. The leaves are from 0·00008 to 0·0002 mm. thick.

Production of gold.—The annual production of gold, after remaining nearly stationary at 5,000,000 or 6,000,000 ozs. for many years, began to rise rapidly in 1891 and amounted to 22,850,000 ozs. of the value of 97,100,000*l.* in 1915. It is now declining, partly owing to the exhaustion of some of the mines, and partly owing to the rise in prices which has made the working of the poorer mines unprofitable. Many countries contribute to the output, and of these the Transvaal, United States, Australia, Mexico, Rhodesia, India, and Canada between them are responsible for 90 p.c. of the world's production. The British Empire produces over 60 p.c, of the total amount. The world's stock of gold is estimated at 1,800,000,000*l.*

Bibliography.—A full bibliography of gold is appended to the Metallurgy of Gold, by T. K. Rose, 6th edit., London, 1915. The following are among the most important treatises on the metallurgy of gold published of late years: The Stamp Milling of Gold Ores, by T. A. Rickard, New York and London, 3rd ed., 1901; Ore Dressing, by R. H. Richards, New York, 1903; Cyaniding Gold and Silver Ores, by H. F. Julian and E. Smart, London, 1904; Gold Dredging, by C. C. Longridge, London, 1905; Rand Metallurgical Practice. T. K. R.

COMPOUNDS OF GOLD.

Two oxides are known, the monoxide or suboxide Au_2O, and the sesquioxide or peroxide Au_2O_3 (Bullnheimer, Chem. Zentr. 1897, i. 522; Vanino, Ber. 1905, 38, 462). Auroauric oxide $(AuO)n$ is formed by the partial decomposition of auric hydroxide at 160°.

The *hydroxide* $Au(OH)_3$ is best prepared by heating a solution of gold chloride with magnesia, and washing the residue with nitric acid. It may be obtained pure by reducing potassium auribromide, $KAuBr_4$, with sulphurous acid, and then warming with dilute potassium hydroxide.

It possesses a yellow, olive-green, or brown colour (according to the method of preparation) while damp, and becomes brownish or black on drying. When warmed with alcoholic potash, metallic gold is precipitated in minute scales, used in *miniature painting*.

The hydroxide is soluble in potash, with formation of a very unstable *potassium aurate.* The solution may be used in electrogilding.

The alkali earth aurates have also been obtained. They are stable when dry, but decompose readily in solution under the influence of heat or light. With organic matter they yield explosive powders (Meyer, *l.c.*). When a sheet of gold is used as a positive electrode in sulphuric or nitric acid, a reddish-brown explosive powder, probably a hydroxide of gold, is formed (Hampe, Chem. Zeit. 14, 1778).

When acted upon by ammonia, the oxide produces a green or brown *fulminate* allied to that of silver. The fulminate may be obtained as a buff-coloured precipitate, containing some ammoniacal subchloride of gold, on addition of ammonia to gold chloride solution. For a description of the explosive nitrogenous compounds of gold obtained from auric hydroxide and the salts of gold by the action of ammonia or ammonium carbonate, *see* Weitz (Annalen, 1915, 410, 117).

Aurous sulphide Au_2S is formed when sulphuretted hydrogen is passed into an acidified solution of gold cyanide or chloride. It is a brown powder, soluble in water when moist, and forms double salts with potassium and sodium sulphites (Ditte, Compt. rend. 1895, 120, 320; Antony and Lucchesi, Gazz. chim. ital. 1896, 26, ii. 350).

Auroauric sulphide Au_2S_2 is formed by passing sulphuretted hydrogen into a cold neutral solution of gold chloride (Antony and Lucchesi, Gazz. chim. ital. 1889, 19, 545; 1891, 21, ii. 209; Christy, J. Soc. Chem. Ind. 1897, 332).

Auric sulphide Au_2S_3 is obtained as a deep yellow precipitate, by treating anhydrous lithium aurichloride with sulphuretted hydrogen at −10° (Antony and Lucchesi, Gazz. chim. ital.

1890, 20, 601, and *l.c.*). It is a graphitic amorphous powder, sp.gr. 8·754 and decomposes at 197°-200° into its elements. Caustic alkalis and hydro- and poly- sulphides of ammonia decompose it with deposition of metallic gold. The three sulphides form colloidal solutions in alcohol.

When finely divided gold is heated with sulphur and potassium carbonate, a double sulphide of potassium and gold, which resists a red heat and is soluble in water, is obtained. It is employed for the production of *Burgos lustre* in gilding china.

Various gold sodium, potassium, and ammonium sulphites and thiosulphites have been obtained (Antony and Lucchesi, *l.c.*). The sulphites, $K_5[Au(SO_3)_4],5H_2O$; $Na_5[Au(SO_3)_4],14H_2O$; $Au_3(SO_3)_4,4NH_3,4H_2O$; and

$$Au(SO_3)_3K_3,2NH_3,2H_2O$$

are described by Pritze (Zeitsch anorg Chem. 1908, 59, 198), whilst the compound $AuS_3{\cdot}NH_4$ has been prepared by Hofmann and Höchtlen (Ber. 1903, 36, 3090; 1904, 37, 245).

Thiosulphate of gold and sodium

$$Au_2S_2O_3,3Na_2S_2O_3,4H_2O$$

crystallises in colourless needles, freely soluble in water. It is formed by the action of sodium thiosulphate on gold chloride. This salt exists in combined fixing and toning photographic baths.

Aurous chloride $AuCl$ is formed by heating the trichloride at 170°-180°. It is a yellowish powder, sp.gr. 7·4, which combines with chlorine at ordinary temperature forming auric chloride and decomposes into its elements at about 185° (Rose, Chem. Soc. Trans. 1895, 881, 905; Campbell, Trans. Faraday Soc. 1907, 3, 103). It is insoluble in water, but decomposed by it with the formation of auric chloride and metallic gold. It dissolves in a solution of potassium bromide forming metallic gold and potassium aurichloride and bromide (Lengfeld, Amer. Chem. J. 1901, 26, 324). Liquid ammonia reacts on aurous chloride forming $AuCl,12NH_3$ which loses ammonia on warming and yields $AuCl,3NH_3$, which when heated to 180° is decomposed with formation of ammonium chloride and gold (Meyer, Compt. rend. 1906, 143, 280).

Auric chloride or **trichloride** $AuCl_3$ is prepared by dissolving gold in *aqua regia* and evaporating the solution to dryness at a temperature below 120°, the hydrochloric acid being always kept in excess over the nitric acid

$$Au+HNO_3+4HCl=HAuCl_4+2H_2O+NO$$

The residue is dissolved in water and filtered from the aurous chloride which is always produced, and the solution is evaporated on the water-bath. Large orange-coloured efflorescent crystals of the hydrated chloride $AuCl_3,2H_2O$ are thus produced.

According to Thomsen, the chloride is best prepared as follows. Powdered gold is converted by the action of chlorine into the dark red crystalline dichloride, and a little water is added to convert it into a mixture of mono- and trichlorides. The mass is heated gently to decompose the former, and the residue is dissolved in water, filtered from the reduced metal, evaporated and heated to 150°, with production of a brown crystalline mass of the anhydrous chloride. The chloride is also formed when gold is treated with fuming hydrochloric acid in the presence of a trace of manganous chloride and the mixture is exposed to light (Berthelot, Compt. rend. 1904, 138, 1297).

If gold is treated with liquid chlorine in a sealed tube at the ordinary temperature, the metal is converted into a crystalline red mass, but when heated at 100°, the gold dissolves entirely, forming a deep yellow solution from which, on cooling, auric chloride separates in wine-red hygroscopic crystals.

Between 170° and 240° auric chloride dissociates into aurous chloride and chlorine (Meyer, Compt. rend. 1901, 133, 815; Rose, *l.c.*).

Under the influence of heat or light, auric chloride is decomposed in solution, thus:

$$AuCl_3+2H_2O=AuCl+2HCl+H_2O_2$$

and $3AuCl=2Au+AuCl_3$ (Sonstadt, (Chem. News, 1898, 77, 74; Chem. Soc. Proc. 1898, 179; Löwe, Dingl. poly. J. 279, 167). Manganous and uranous sulphate and also manganous chloride reduce gold chloride in the dark, precipitating metallic gold. The process is accelerated in the former case by heat, in the two latter by sunlight (Oechsner de Coninck, Bull. Acad. Roy. Belg. 1902, 316).

Gold chloride is also reduced by charcoal thus:

$$4AuCl_3+6H_2O+3C=4Au+12HCl+3CO_2$$

(Avory, J. Soc. Chem. Ind. 1908, 255; Hay and Tennent, Amer. Chem. J. 1909, 31, 461); by acetylene (Mathews and Watters, J. Amer. Chem. Soc. 1900, 22, 108); and by sulphuretted hydrogen under certain conditions (Schneider, Ber. 1891, 24, 2241; Antony and Lucchesi, Gazz. chim. ital. 1889, 19, 545).

When heated to 200°, the trichloride is resolved into a mixture of aurous chloride and gold. At a higher temperature the whole of the chlorine is given off.

Auric chloride is freely soluble in water, alcohol, and ether. It forms a crystalline compound, $AuCl_3,HCl,4H_2O$, with hydrochloric acid, and forms double chlorides with the alkali metals and with organic bases (Lainer, Monatsh. 11, 220). Auric chloride combines with silver chloride in presence of ammonium chloride to form a purplish-brown salt, in orthorhombic crystals, $3AgCl,4AuCl_3,8NH_4Cl$, readily decomposed by water with the formation of chloro auric acid and silver chloride (Pollard, Chem. Soc. Trans. 1920, 99).

Auric chloride and the sodium and potassium salts, such as $NaCl,AuCl_3,2H_2O$, are employed for toning silver prints in photography (Kebler, J. Franklin Inst. 1900, 150, 235; Johnson, J. Soc. Chem. Ind. 1901, 210). Other alkali double chlorides are described by Wells and Wheeler (Amer. J. Sci. [3] 44, 157).

Gold chloride forms salts with pyridine, such as $C_5H_5N,AuCl_3$, $(C_5H_5N)_2AuCl_3$ (François, Compt. rend. 1903, 136, 1557). Aurophosphorous chloride $(AuPCl_3)Cl$ and complex organic compounds of phosphorus and gold chloride are described by Levi Malvano (Atti R. Accad. Lincei, 1908, [v.] 17, i. 847). The acetates and succinates are used in photography (Mercier, Brit. Journ. Phot. 39, 354).

Chloroauric acid $AuCl_3,HCl$, prepared by the action of chlorine on gold suspended in hydrochloric acid (Lengfeld, Amer. Chem. J. 1901, 26, 324), reacts with silver nitrate, forming a brown precipitate, $Au(OH)_3,4AgCl$, which, with ammonia, forms gold fulminate, $Au(OH)_2NH_2$ or $AuN,2H_2O+H_2O$. Gold fulminate is very explosive when dry, and when heated with potash forms a flocculent brownish-black product, probably $Au(HO)_2{\cdot}NH{\cdot}Au(OH)_2$, which is still more explosive (Jacobson, Compt. rend. 1908, 146, 1213; *cf.* Weitz, Annalen, 1915, 410, 117). Chloroauric acid forms salts such as $KAuBr_4$, &c. (Longfeld, *l.c.*).

By the action of aurochloric acid on sodium azoimide an orange crystalline very explosive compound is obtained (Curtius and Rissom, J. pr. Chem. 1898, [ii.] 58, 261).

Chloroauric acid gives a bright yellow colour with a hydrochloric acid solution of *o*-tolidine. This solution, which forms a delicate colour test for the presence of free chlorine in water, has been shown by Pollard (Analyst, 1919, 94) to form a delicate test for the presence of gold; 1 part of gold in 20 million parts of water can thus be detected in a depth of 10 cms. of liquid.

Aurous bromide AuBr is a greenish-yellow powder, which is formed by heating auribromic acid at 115°. Its properties are very similar to those of the corresponding chloride (Meyer, *l.c.*).

Auric bromide $AuBr_3$ is formed by the action of dry bromine on powdered gold; when heated it dissociates forming the monobromide (Meyer, Compt. rend. 1909, 148, 346) According to Lengfeld (*l.c.*), aurous bromoaurate Au_2Br_4 also exists. Bromoauric acid and bromoaurates have also been prepared.

Aurous iodide can be prepared by the action of excess of pure iodine on metallic gold above 50°, the excess of iodine being then removed by careful sublimation (Meyer, Compt. rend. 1904, 139, 733). It is also formed by the action of hydriodic acid on gold oxide. It is a white powder, turning green in air and decomposing at 190°; it is also decomposed by solvents such as chloroform. With liquid or gaseous ammonia, it forms $AuI,6NH_3$ and AuI,NH_3 (Meyer, *ibid.* 1906, 143, 280). Auric iodide probably does not exist.

Gold fluoride has been described by Lenher (J. Amer. Chem. Soc. 1903, 25, 1136).

Gold chromate can be obtained by treating silver chromate with auric chloride: $Au_2(CrO_4)_3$ is obtained in solution, whilst the chromate $Au_2(CrO_4)_3CrO_3$ crystallises from the mother liquor (Orloff, Chem. Zeit. 1907, 31, 1182).

When solutions of sodium aurate and chromate are mixed, sodium aurochromate containing excess of chromate is obtained, the solution of which forms an excellent toning bath, giving purple-bluish tones. It is neutral and can be kept, and the yellow colour allows the toning to be done in daylight (Mercier, Chem. Zeit. Rep. 24, 272; J. Soc. Chem. Ind. 1900, 1038).

Gold carbide. Au_2C_2 is formed by passing acetylene into aurous thiosulphate. It is very explosive when dry and is decomposed by hydrochloric acid, forming acetylene and aurous chloride. Treated with water it yields gold and carbon (Mathews and Watters, *l.c.*).

The following gold salts have also been obtained: arsenates (Stavenhagen, J. pr. Chem. 1895, [2] 51, 1); selenates and tellurates (Lenher, J. Amer. Chem. Soc. 1902, 24, 354, 355, 918); various alkyl gold chlorides (Pope and Gibson, Chem. Soc. Trans. 1907, 2061); thiocarbamides (Moir, *ibid.* 1906, 1345); mercaptides (Herrmann, Ber. 1905, 38, 2813), and other complex organic compounds (Dunstan and Shepheard, Chem. Soc. Proc. 1893, 212; Weigand, Zeitsch. angew. Chem. 1906, 19, 139; Averkieff, J. Russ. Phys. Chem. Soc. 1908, 40, 840).

The thio- compounds of certain resins and ethereal or fatty oils or thioacids, yield compounds with gold which are soluble in most organic solvents and which can be employed in the ceramic enamel and glass industries for the deposition of the finest layers of bright metal on various substances (Pertsch, Frdl. 1894–97, 1324).

According to Odenheimer (J. Soc. Chem. Ind. 1892, 600), textile fabrics padded or printed with a gold salt and then treated with a reducing agent assume a beautiful grey colour, the process being accelerated by heat or sunlight. The shade depends on the nature of the reducing agents employed and on the strength of the gold solution. When these grey fabrics are subjected to heat between rollers, red, purple, or pink colours are obtained, depending on the original shade of grey. The high price of gold is no disadvantage in this process as only a very minute quantity of gold solution is required. Thus, for a beautiful pearl-grey on half silk, the cost is only ¾*d.* per lb. of material dyed.

Gold cyanides (*see* ELECTROPLATING and CYANIDES).

GOLD, MANNHEIM. A brass containing 80 p.c. of copper and 20 p.c. of zinc.

GOLD, MOSAIC. A fine, flaky yellow form of tin disulphide; is used in the arts to imitate bronze under this title, and is preferably prepared as follows. A mixture of 7 parts of sulphur, 6 parts of ammonium chloride, and 18 parts of a powdered amalgam containing 2 parts of tin to 1 part of mercury, is heated gently until the smell of sulphuretted hydrogen is no longer perceptible. The heat is then raised to low redness, and a mixture of mercurous chloride, ammonium chloride, and cinnabar sublimes, while the mosaic gold alone remains. A fine product is also obtained by heating a mixture of 5 parts of stannous sulphide and 8 parts of mercuric chloride.

The essential point is that tin must be present in a volatile form; stannous chloride itself may be used.

A pale-yellow mosaic gold is produced by heating 50 parts crystalline stannous chloride with 25 parts flowers of sulphur; a reddish-yellow product is obtained on heating together 50 parts 50 p.c. tin-amalgam, 25 parts stannous chloride, 35 parts ammonium chloride and 35 parts of sulphur. 57 p.c. of the tin taken is obtained as the sulphide (Lagutt, Zeitsch. angew. Chem. 1897, 557).

The temperature should not be too high, as the stannic sulphide, when strongly heated, loses one equivalent of sulphur and becomes black.

Mosaic gold is insoluble in nitric and hydrochloric acids, but dissolves in *aqua regia* and in alkaline hydroxides.

A brass, introduced by Hamilton and Parker (Edinb. J. of Sc. 1826), and containing 52 to 55 p.c. of zinc, is also known by this name. A nixture of equal parts of zinc and copper is used at the lowest possible temperature, and zinc is slowly added, with constant stirring, until the desired colour is produced. The colour passes from a brassy yellow to a purple or violet, and finally becomes perfectly white. The mass, when cooled, has the colour of gold, and is said to be not liable to tarnish.

GOLD, ORANGE, *v.* AZO-COLOURING MATTERS.

GOLD PURPLE (*Purple of Cassius*). This compound is obtained as a fine, flocculent purple precipitate on addition of a solution of stannous chloride containing stannic chloride, to a dilute neutral solution of gold chloride. The presence of the stannic chloride is essential, as pure stannous chloride produces only a brown precipitate.

A very fine product is obtained by adding stannous chloride to ferric chloride until the solution is of a pale green colour, and employing the mixture to precipitate the gold solution. According to another process, 1 part of tin is dissolved in the minimum of hydrochloric acid, and 2 parts of the tin are dissolved in a cold mixture of 3 parts of nitric acid and 1 part of hydrochloric acid, the solution being finally heated to ensure conversion of all the tin into stannic chloride. A solution of 7 parts of gold in a mixture of 6 parts of hydrochloric acid and 1 part of nitric acid is diluted with 3,500 parts of water, and the solution of the stannic chloride is added, the stannous chloride being then added in drops until the required colour (from violet to purple or brown) is obtained (Baisson).

According to Pelletier, a purple of Cassius of constant composition is obtained as follows. A solution of as much gold chloride as contains 20 grains of gold is diluted to 700 or 800 c.c., and tin filings are introduced. The liquid speedily becomes brown and turbid, and finally deposits the purple, which is washed and dried. It is said to contain 32·75 p.c. of stannic oxide, 14·62 p.c. of stannous oxide, 44·77 p.c. of aurous oxide, and 7·86 p.c. of water.

Purple of Cassius may also be obtained in great beauty by treating an alloy of gold 2 parts, tin 3·5 parts, and silver 15 parts, with nitric acid to remove the silver and oxidise the tin.

Zsigmondy (Annalen, 301, 361) prepares purple of Cassius by mixing 200 c.c. of gold chloride (3 grams Au per litre) with 250 c.c. stannous chloride (3 grams Sn per litre) and 4 litres of water. After 3 days, the purple is deposited, leaving a liquid free from gold and tin. The precipitate thus prepared contains, after ignition, 40·3 p.c. gold and 59·7 p.c. stannic oxides.

According to Moissan (Compt. rend. 1905, 141, 977), when gold-tin alloys are distilled in air, a finely divided mixture of stannic oxide, lime, and gold is obtained, having the colour and properties of purple of Cassius. Similar deposits of varying tint can be obtained by substituting for lime other oxides such as zirconia, silica, magnesia, or alumina.

Schneider (Zeitsch. anorg. Chem. 1893, 5, 80) obtained an aqueous solution of gold purple by treating an alloy of gold, tin, and silver with concentrated nitric acid. When the resulting black powder is washed with ammonia, a ruby-red coloured solution is obtained, which is dialysed until it contains no more ammonia. It contains 0·5800 gram of gold and 5·4048 grams of stannic oxide per litre.

Potassium cyanide decolorises the solution and stannic acid separates. With mercury, the solution becomes brownish-red and gold is extracted; whilst with excess of hydrochloric acid, the solution becomes violet and yields finely divided gold on dialysis. According to this author, the soluble form of purple gold is, possibly, a mixture of the hydrosols of gold and stannic acid.

This body, which is used in the manufacture of artificial gems (*v.* GEMS, IMITATION AND COUNTERFEIT), and for imparting a red, rose, or pink colour to porcelain or enamel, varies in colour from a violet to a purplish-red or brown. The dry precipitate is insoluble in strong or dilute alkalis, but when moist the purple dissolves in water in the presence of very small quantities of acids and alkalis. Salts and excess of alkalis and acids precipitate the purple from these solutions.

While moist, it is also soluble in ammonia with production of a purple colour, from which the precipitate is redeposited on addition of an acid or on boiling, and, in the latter case, is not again soluble. The ammoniacal solution precipitates gold on exposure to light. The purple does not pass through the membrane of a dialyser.

When dried and triturated, the purple of Cassius acquires a metallic lustre. No gold is removed from it by the action of mercury. It retains water at 100°, but gives it up and acquires a brick-red colour when ignited, and loses its colour at the melting-point of gold, but without evolution of oxygen.

On adding a greater quantity of mercurous chloride to a solution of auric chloride than that required for the reaction

$$3HgCl+AuCl_3=3HgCl_2+Au,$$

the characteristic colour of purple of Cassius is obtained. If barium sulphate suspended in water is previously mixed with the mercurous chloride, the sulphate takes up the gold and becomes the colour of the purple. Antony and Lucchesi (Gazz. chim. ital. 1896, ii. 195) therefore regard true purple of Cassius as being, not a compound, but merely stannic acid mechanically covered with gold.

The constitution of this substance, of which the composition, as found by analysis, is very variable, is not yet established. Berzelius, judging from the researches of Figuier, considered it to be a hydrated stannate of gold and tin. Macquer looked upon it as a mixture of stannic hydroxide and metallic gold; and Proust considered it to be a mixture of aurostannous stannate and stannic hydroxide.

Zsigmondy regards the purple as a mixture of colloidal gold and colloidal stannic acid; the gold acquiring the property of dissolving in very dilute acids through the presence of the stannic acid which is soluble in them. A mixture of colloids may thus behave as a chemical individual where the properties of one of the constituents may be completely hidden.

Debray (Compt. rend. 75, 1025), and also Moissan (*l.c.*), look upon it as allied to the *lakes*, and as consisting of gold combined with stannic acid, in the same way as the colouring matter of the lake is combined with alumina, the gold being insoluble in mercury, as the colouring matter is insoluble in water. Debray has prepared the purple by boiling freshly precipitated stannic hydroxide with a mixture of gold chloride and potassium oxalate. The action of ammonia on the purple is similar to its action on stannic hydroxide, both being soluble while moist, but becoming insoluble when anhydrous.

The fact that the ammoniacal solution precipitates gold is in favour of the view that the gold is present in the metallic state, as ammonia is not known to precipitate precious metals by action on their oxides.

Debray has also produced a purple by replacing the stannic hydroxide by alumina.

Müller (J. pr. Chem. [ii.] 30, 252) has prepared purples by several processes without the use of tin. A pale rose (containing 0·1 p.c. of gold) to deep carmine pigment is produced by igniting a well washed and dried mixture of magnesium oxide and gold chloride. A similar result is obtained by heating the mixture in a current of hydrogen.

Lime, calcium carbonate, calcium phosphate, barium sulphate, and lead and zinc oxides give similar but less satisfactory results.

The most intense purple is, however, obtained by reducing a mixture of aluminium hydroxide and gold chloride with alkaline grape-sugar solution. The mixture is agitated and heated until of a bright scarlet colour, but the colour must not be allowed to reach a purplish red, or the resultant product will be of inferior brilliancy.

Similar but less brilliant purples than those with magnesia and alumina are obtained with tin. As much stannous chloride as corresponds with 9 grams of stannic oxide, is dissolved in 200 c.c. of water, and the solution is rendered alkaline by addition of potassium carbonate. Grape sugar solution is added, and the mixture is diluted to 300 litres, and is warmed until of the best colour.

These methods of preparation uphold the view that the gold is present in the metallic state.

Red, blue, violet, and green colloidal solutions of gold can be readily prepared. Colloidal solutions of gold can be formed by the addition of gold chloride solution to water, containing small quantities of the following substances: turpentine oil, pinene, rosemary oil, or potassium carbonate with formaldehyde, pinene, turpentine oil, or alcohol. The formation of the colloidal solution can be accelerated by adding to the gold chloride solution a few drops of gold solution already in the colloidal state. The colour of the solutions depends on the temperature and the concentration (Vanino and Hartl, Ber. 1905, 38, 463; 1906, 39, 1696; Zsigmondy, Zeitsch. physikal. Chem. 1906, 56, 65; Henrich, Ber. 1903, 36, 609; Garbowski, *ibid.* 1215). Colloidal gold can also be precipitated by the action of formaldehyde or acetaldehyde on gold chloride in the presence of sodium hydroxide (Zsigmondy, Annalen, 1898, 301, 29; Zeitsch. Chem. Ind. Kolloide, 1907, i. 272) or potassium carbonate (Thomas, J. pr. Chem. 1909, 80, 518).

Carey Lea (Zeitsch. anorg. Chem. 1897, 13, 447) obtained a beautiful green solution by mixing a 10 p.c. sodium hyposulphite solution with 1 c.c. of gold chloride solution (10 c.c. =1 gram gold) and a drop of sulphuric acid. As soon as the solution begins to darken, 30 c.c. of water are added. Gradually, a bluish-black precipitate of metallic gold separates; after filtration, the green solution again becomes turbid. If the solution is shaken and allowed to remain, a precipitate of gold is deposited on the sides of the vessel, which is yellowish brown by reflected light and bright blue by transmitted light.

Humic acid, added to gold chloride, produces colloidal gold solutions of various colours, depending on the conditions of the experiment (Ehrenberg and Pick, Zeitsch. chem. Ind. Kolloide, 1909, 5, 30).

When 1 litre of water containing 1 gram of auric chloride and made just alkaline with sodium carbonate, is boiled, and then poured into 300 c.c. of a cold solution of catechol (pyrocatechin) containing 11 grams per litre, a red coloration is produced, rapidly turning to violet. On mixing 10 such preparations and just acidifying with sulphuric acid, the liquid becomes blue and deposits a blue powder which is washed with water, then with alcohol, is dissolved in ammonia and can be reprecipitated by sulphuric acid. The substance manifests acid properties, forming salts with some of the heavy metals (Henriot, Compt. rend. 1904, 138, 1044).

A stable solution of colloidal gold of therapeutic value is obtained by reducing with atoxyl (*p*-aminophenylarsinate) a gold chloride solution made faintly alkaline with sodium hydrogen carbonate. Similar solutions are also obtained by reduction with sodium sulphanilate or naphthionate. When evaporated to dryness in a vacuum, a grey residue is obtained which dissolves completely in water, forming a characteristic ruby-red solution of colloidal gold (Poulenc Frères, D. R. P. 206343).

Red to purple colloidal solutions may be obtained by passing carbon monoxide, pure, or mixed with carbon dioxide, through a solution of auric chloride in conductivity water, containing 0·002–0·05 p.c. gold (Donau, Monatsh. 1905, 26, 525). Similar solutions have also been obtained by reducing very dilute solutions of gold chloride with phenylhydrazine hydrochloride (Gutbier and Resenschek, Zeitsch. anorg. Chem. 1904, 39, 112), hydrazine hydrate (Gutbier, *ibid.* 1902, 31, 448), hydroxylamine hydrochloride (*ibid.* 1902, 32, 347), or with sodium lysalbate or protalbate (Paal, Ber. 1902, 35, 2236), quinol, gallotannic acid, *p*-oxyphenylaminoacetic acid, 1:2:4-diaminophenol and other photographic developers. Some of these colorations are so intense that they may be used as delicate tests for gold (Saul, Analyst, 1913, 54); also by the action of *Aspergillus oryzæ* on 0·01 gram gold chloride in 100 c.c. water (Vanino and Hartl, *ibid.* 1904, 37, 3620). An electric discharge between gold poles also gives reddish-purple or dark blue solutions, which can be filtered without change and retain their colour for months (Bredig, Zeitsch. angew. Chem. 1898, 951; Bredig and Reinders, Zeitsch. physikal. Chem. 1901, 37, 323). Various other methods of preparing colloidal gold solutions and precipitates have been proposed (Schottländer, Chem. Zentr. 1894, ii. 409; Brunck, Annalen, 1903, 327, 240; Donau, Monatsh. 1904, 25, 545; Whitney and Blake, J. Amer. Chem. Soc. 1904, 26, 1339;

Vanino and Hartl, Chem. Zentr. 1907, i. 1099; Vanino, *ibid.* 1908, i. 446; Dauvé, J. Pharm. Chim. 1909, 29, 241; Doerinckel, Zeitsch. anorg. Chem. 1909, 63, 344; Hartwagner, Kolloid. Zeitsch. 1915, 16, 79; Zsigmondy, Elektrochem. 1916, 22, 102).

Gold chloride solution, with water glass and formalin heated on the water-bath gives, according to quantity, bright red, claret-red, blue, or even green colloidal solutions. Very small amounts of gold gave a rose-red coloration (Kuspert, Ber. 1902, 35, 4070).

According to Stenberg (Ann. Physik. 1908, [iv.] 26, 329), the various colours of colloidal gold solutions are due to the difference in form of the particles. Distinct forms of particles exist for the red and blue solutions; the violet colour is produced by a mixture of these, whilst green solutions are due to the condensation of the particles which give rise to the red and blue colour.

The liquid hydrosols of gold are decolorised when shaken with animal charcoal, barium sulphate, powdered porcelain, amorphous silica, fibres of filter paper or with electrolytes, but if gum arabic or gelatin is present, this reaction is prevented or diminished (Donau, Monatsh. 1905, 26, 525). An electric current in the presence of various electrolytes changes the red colloidal solutions into blue (Blake, Amer. J. Sci. 1903, [iv.] 16, 433).

Silk and cotton fibres treated with tannin or stannous chloride and pyrogallol, are coloured red and blue respectively, on addition of gold chloride. This colour is destroyed by concentrated acids, free halogens, and reducing agents, but not by dilute acids or alkalis.

GOLD, YELLOW, *v.* VICTORIA YELLOW.

GOLDEN YELLOW *v.* NAPHTHALENE.

GOMAINE. Trade name for a solution of iodoform and camphor in sesamé oil.

GOMART RESIN *v.* OLEO-RESINS.

GOOSEBERRY. The fruit of *Ribes grossularia* (Linn.). There are many varieties, differing in shape, size, texture, and colour.

They are largely used, both immature and ripe, in cookery, as raw fruit and in jam making. The average composition, deduced from 34 analyses, is given by König as follows:—

Water	Protein	Free acid	Invert sugar	Saccharose	Other carbohydrates	Fibre	Ash
83·6	0·5	1·4	7·1	0·9	0·6	3·5	0·4

The acidity is chiefly due to malic acid.

H. I.

GORNEROL. Trade name for an essential oil prepared from the leaves of *Melaleuca leucadendron* (Linn.) (Nat. Ord. *Myrtaceæ*) of New Caledonia, similar to, if not identical with, oil of Cajuput (*q.v.* under art. OILS, ESSENTIAL). Known also as Niaouli oil.

GORSE, called also **FURZE** and **WHIN.** *Ulex europæus* (Linn.). A plant belonging to the *leguminosæ*, and therefore capable, by the aid of symbiotic bacteria, of fixing atmospheric nitrogen.

It will grow in soils poor in mineral matter, and has been strongly recommended as a fodder plant, for littering, and as a green manure. It is estimated that a crop of 20,000 kilos. per hectare may be obtained, and that this, in feeding value, is equal to 8000 kilos. of hay.

Average composition, according to Girard (Ann. Agron. 1901, 27, 5):

Water	Protein	Fat	N-free extract	Cellulose	Ash
52·7	4·6	0·9	26·0	14·5	1·6

The N-free extract includes about 1·4 p.c. sugar, 9 p.c. pentosans, and 1·6 p.c. pectin.

The ash contains:

K_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3
27·1	11·7	4·3	2·4	6·7	4·7

With horses the digestion coefficients obtained were as follows: Ash 40, fat 22, protein 56, cellulose 43, sugar 100, total non-nitrogenous matter 55. With sheep the figures were lower. Only the tender young shoots are readily eaten by animals, unless the material be well crushed, so as to soften and break the prickles.

Experiments in 1899 and 1901 by Voelcker (Jour. Roy. Agric. Soc. for these years) showed that with sheep, gorse, properly comminuted by special machinery, could, with advantage, replace a portion of the roots used in feeding. Not more than 9 or 10 lbs. of gorse per head, per week, however, could be used.

H. I.

GOSLARITE, *Zinc-vitriol*, or *White vitriol.* Hydrated zinc sulphate $ZnSO_4,7H_2O$, crystallised in the orthorhombic system and isomorphous with epsomite. It results from the weathering of zinc-blende, and usually forms white encrusting masses, or sometimes aggregates of fine, silky fibres. Being readily soluble in water it is not of common occurrence, but is occasionally found in the old galleries of zinc mines. Considerable quantities were at one time obtained from the Rammelsberg mine near Goslar in the Harz Mountains. Varieties are ferro-goslarite and cupro-goslarite.

L. J. S.

GOSSYPITRIN *v.* GLUCOSIDES.

GOSSYPOL. A toxic principle contained in cotton seed and present in glands in all parts of the cotton plant but the woody tissues; gives a blood-red solution in sulphuric acid, and a blue coloration when its alkaline solution is exposed to the air. Is found in commercial cold-pressed cotton-seed oil to the extent of 1·5 p.c., but not in the 'hot-pressed' oil, as the gossypol is then oxidised and most of it remains in the cake (Carruth, J. Amer. Chem. Soc. 1918, 40, 647).

GOUDANG WAX *v.* WAXES.

GOULARD'S EXTRACT, LOTION, WATER. Solutions of basic lead acetate.

GRAHAMITE. A variety of bitumen allied to gilsonite (*q.v.*).

GRAIN LAC *v.* *Lac resins*, art. RESINS.

GRAIN OIL *v.* FUSEL OIL.

GRAIN TIN *v.* TIN.

GRAINS OF PARADISE *v.* COCCULUS INDICUS.

GRANITE. An acid igneous rock consisting of a granular (hence the name) holocrystalline aggregate of quartz, felspar, and mica. It contains about 65–75 p.c. of silica, which is present partly as free silica (quartz forming 30–50 p.c. of the rock), and partly in combination in the silicates. The felspar (36–68 p.c.) is generally a potash-felspar, usually orthoclase, but sometimes microcline; it may also, especially in the 'soda granites,' be a soda-bearing orthoclase, anorthoclase, or a plagioclase (albite to oligoclase). The mica (5–18 p.c. of the rock) is usually of two kinds, a white mica, muscovite, and a black mica, biotite.[1] The one-mica granite biotite-granite is sometimes distinguished as granitite. Less frequently, hornblende or augite may partly or wholly take the place of mica, as in hornblende-granite and augite-granite. In other varieties, especially those altered by pneumatolytic agencies, tourmaline may be present. Granites differ widely in their general appearance and character, due to variations in their coarseness of grain, the occasional presence of larger porphyritic crystals embedded in a finer-grained groundmass, the colour of the felspars (dull white to pink), the lack or predominance of the dark-coloured minerals, biotite, and hornblende. Sp gr. 2·6–2·8; weight per cubic foot, 160–175 lb.; crushing strength, 1000–2000, or sometimes even 3000, tons per square foot. Degree of porosity very low, 0·2–0·3 p.c. The grain of the rock is sufficiently coarse for the individual minerals to be distinguishable by the unaided eye. It varies from fine grained in aplite (a variety composed of only quartz and felspar) to very coarse grained in pegmatite and graphic granite (the latter characterised by an intimate intergrowth of quartz and felspar). At times granite displays a more or less pronounced foliated structure (gneissose granite), passing imperceptibly into gneiss. This rock has the same mineral and chemical composition as granite, and to a certain extent can be employed for the same purposes.

The following analyses are of: I, Coarse-grained, red biotite-granite from Peterhead, Aberdeen (J. A. Phillips, 1880). II, Fine-grained, bluish-grey muscovite-biotite-granite from Rubislaw, Aberdeen (W. Mackie, 1901). III, Biotite-granite with large porphyritic crystals of red felspar from Shap, Westmorland (J. B. Cohen, 1891). IV, Grey muscovite-biotite-granite from Gready near Luxullian, Cornwall (J. A. Phillips, 1880). V, Dark red, medium-grained hornblende-biotite-granite from Mount Sorrel, Leicestershire (C. K. Baker). VI, Average of nine analyses of the grey, two-mica granites, of Leinster, S.E. Ireland (S. Haughton, 1855). For a large collection of analyses of granite, *v.* J. Roth, Beitrage z. Petrographie d. plutonische Gesteine, Berlin, 1873–84; H. S. Washington, U.S. Geol. Survey, Prof. Paper, 1917, No. 99.

	I.	II.	III.	IV.	V.	VI.
SiO_2 .	73·70	69·01	68·55	69·64	67·16	72·08
Al_2O_3 .	14·44	17·74	16·21	17·35	16·19	14·46
Fe_2O_3 .	0·43	0·97	2·26	1·04	3·82	2·40
FeO .	1·49	2·05	n.d.	1·97	—	—
MnO .	trace	—	0·45	trace	—	—
CaO .	1·08	1·95	2·40	1·40	2·59	1·76
MgO .	trace	0·48	1·04	0·21	1·58	0·10
K_2O .	4·43	3·94	4·14	4·08	5·38	4·80
Na_2O .	4·21	2·73	4·08	3·51	2·43	3·01
P_2O_5 .	trace	—	—	trace	—	—
H_2O .	0·61	1·18	n.d.	0·72	1·02	0·91
	100·39	100·05	99·13	99·92	100·17	99·52
Sp.gr. .	2·69	2·61	2·69	2·72	2·66	2·63

Granites are of wide distribution as rock-masses of considerable magnitude. They are extensively developed and quarried in Cornwall and Devon, where they occur as a series of bosses protruding through the killas or clay-slate. The largest of these intrusions are, proceeding westwards, those of Dartmoor, Brown Willy or Bodmin Moor, St. Austell or Hensbarrow, Carn Menelez or Penryn, and the Land's End or Penzance districts. In addition to these principal exposures there are numerous smaller masses. The granite of Devon and Cornwall is usually grey and coarse-grained, but red granite also occurs, as at Trowlesworthy in the western part of Dartmoor. Although used locally since prehistoric times, Cornish granites were not systematically quarried until early in the eighteenth century; one of the first quarries to be developed was the De Lank quarry near Bodmin, which supplied the material for the exterior of the Eddystone lighthouse in 1756. Dartmoor granite was sent to London in 1817 for the construction of Waterloo Bridge, and in 1831 for London Bridge. The granites of Scotland are of great industrial importance. Aberdeen granite was first brought to London for paving in 1764, but the great development of the trade dates from about 1850. The Aberdeen stone, valued for monumental work, is of a grey or blue tint; whilst that of Peterhead is usually of a fine pink colour. The Ross of Mull in Argyllshire furnishes a handsome pink granite, yielding blocks of exceptional size. Granite is also quarried in Kirkcudbrightshire, the grey stone of Dalbeattie being well-known in commerce. Ireland is rich in granites. The very large Leinster mass, in the counties of Dublin, Wicklow, Wexford, and Carlow was quarried as early as 1680. Other important occurrences are in the Mourne Mountains in Co. Down, and in Co. Galway and Co. Donegal. Other British occurrences are in the Scilly Islands, Jersey and Guernsey, Lundy Island, Malvern Hills, Mount Sorrel in Leicestershire, Skiddaw, Eskdale, and Shap in the Lake District, the Sarn district in North Wales, Foxdale and Dhoon in the Isle of Man; and in Scotland many other localities in addition to those mentioned above.

Granite is extensively used as a building and paving stone, and owing to its massive character and durability it is especially useful where massive constructive work is required, as in the foundation of buildings, in docks, sea-walls, piers of bridges, lighthouses, &c. Taking a high polish, which is retained on exposure to weather, and being suitable for carving, it is much in demand for ornamental and monumental work. Refuse from the quarries is dressed as paving setts, curb stones, or crushed and screened for road metal, railway ballast, and granite chips. Partly weathered granite from near the surface, especially when covered by a soil rich in humic acids, shows dull cloudy felspars and the darker silicates have a rusty appearance, and the rock itself is often quite crumbly. This surface weathering may sometimes extend to considerable depths, and under certain conditions china-stone or china-clay may result. The solid fresh rock is, however, little affected by weathering processes when employed as a building stone. The most important cause of disintegration under these conditions is that due to the unequal degree of expansion and contraction of the different minerals with changes of temperature; coarse-grained granites being more affected by this agency than the finer-grained varieties. The handsome coarse-grained Rapakivi granite of Finland lacks durability on this account. Granite has, however, the defect that it does not resist fire well. The cracking and scaling of the surface is due to the presence of vast numbers of microscopic cavities, containing water and liquid carbon dioxide, in the quartz. Stone containing nodules and specks of iron-pyrites should be avoided, since this mineral readily decomposes, producing free acid and unsightly brown stains. Of special varieties used for ornamental purposes mention may be made of luxullianite, and orbicular or spheroidal granite. The former, from Luxulian in Cornwall, consists of large porphyritic crystals of pink felspar set in a black matrix of tourmaline and quartz. A good set of large polished blocks and slabs of orbicular granite from several localities is displayed in the Mineral Gallery of the British Museum (Natural History). Granite was used as an ornamental stone by the ancient Egyptians and the Romans.

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[1] These minerals carry part of the potash, each of them containing about 10 p.c. K_2O. The bulk of the potash is, however, carried by the felspar, pure potash-felspar containing 16·9 p.c. K_2O.

Granite rocks are always divided naturally by joints, which usually run in three directions, approximately at right angles, thus enabling the rock to be quarried in roughly cuboidal blocks. These are sometimes of considerable size, providing, for example, the obelisks up to 100 feet in length obtained by the ancient Egyptians in the quarries of pink hornblende-biotite-granite at Assouan (=Syene) in Upper Egypt. The blocks are split up by 'plug and feather' wedges, the splitting taking place more readily in certain directions, known to the quarrymen as the 'rift' or 'grain' of the stone. This is sometimes due to the presence of flow structure in the rock with a parallelism of the flakes of mica, but at other times it is apparently due to the effect of stresses. When the surface is required to be dressed smooth, it is 'fine-axed' by continual tapping, at right angles to the face, with a special form of axe. Slabs are cut by diamond saws, and columns up to 8 feet in diameter are turned in the lathe with diamond-set tools. The polishing of granite is effected by cast-iron planes worked over the smoothed surface, first with sand and water, and then with emery, the final polish being given with putty powder applied on thick felt. In this way even elaborate mouldings are polished. The name granite is sometimes incorrectly applied as a trade-name to stones of other kinds, *e.g.* 'black granite' to a gabbro or other dark-coloured igneous rock of granitic texture, 'Petit granit' to a black Belgian marble spotted with white encrinites, 'Mendip granite' to a limestone, and 'Ingleton granite' to a conglomerate.

Veins of metalliferous ores frequently occur in connection with granite masses, either in the granite itself or at its junction with the surrounding rocks. Tin ore, in particular, is almost always found only in association with granite. The pegmatite veins occurring in connection with granite often carry various gem-stones (tourmaline, beryl, &c.) and rare-earth minerals.

References.—G. F. Harris, Granite and our Granite Industries, London, 1888. J. Watson, British and Foreign Building Stones, Cambridge, 1911. J. A. Howe, Geology of Building Stones, London, 1910. G. P. Merrill, Stones for Building and Decoration, 3rd ed., New York, 1903. On the granites of the eastern United States, *v.* T. N. Dale, Bull. U.S. Geol. Survey, 1907, No. 313; 1908, No. 354; 1909, No. 404; 1911, No. 484.

L. J. S.

GRANITE BLACK *v.* AZO- COLOURING MATTERS.

GRAPE. The berry of *Vitis vinifera* (Linn.). There are many varieties differing in size, shape, colour, and composition.

König gives as the average percentage composition—

Water	Nitrogenous substances	Free acid	Invert sugar	Other carbohydrates	Fibre	Ash
79·1	0·7	0·7	15·0	1·9	2·1	0·5

The sugar (glucose) in particular is liable to considerable variation, ranging from 9 to 18 or 19 p.c.

This variation, as well as that in the acidity—due to tartaric acid or acid potassium tartrate—is influenced not only by the variety, but also by the climate and soil; a wet winter and a hot, dry summer being generally favourable to the production of sweet grapes, suitable for wine making, whilst much rain during the ripening period dilutes the juice and leads to the bursting and consequent injury of the berries.

The proportion of skin and seeds shows considerable variation in different varieties, averaging about 2·2 p.c. of the whole fruit, and of this the seeds usually constitute about one-fourth. The skin contains tannin, and, according to Malvezin (Compt. rend. 1908, 147, 384), a yellow colouring matter, which, on oxidation either by exposure to air in aqueous solution, or by the action of an enzyme, present in red but absent in white grapes, changes to a red substance.

Sostegni (Gazz. chim. ital. 1902, 32, ii. 17) states that the red colouring matter is a tannin derived from protocatechuic acid and has the formula

$$C_6H_3(OH)_2CO{\cdot}C_6H_3(OH)O{\cdot}C_6H_3(OH)_2.$$

According to Willstätter (Sitzungsber. K. Akad. Wiss. Berlin, 1914, 12, 402), the anthocyanin of grapes—*œnin*, is obtained by digesting grape-skins with acetic acid and adding ether to the extract. The picrate of œnin forms long red prisms, the chloride, prisms with a green glance. Œnin is a monoglucoside of œnidin, $C_{17}H_{15}O_7Cl$.

The skin and seeds of grapes, in a moist condition, were analysed by Balland (Rev. intern. falsif, 1900, 13, 92), who found them to have the following percentage composition—

	Water	Nitrogenous substances	Fat	Soluble carbohydrates	Crude fibre	Ash
Skin .	76·5	1·5	0·9	18·4	2·1	0·6
Seeds .	38·7	5·5	8·6	18·9	27·6	0·7

Wittmann found about 0·4 p.c. pentosans in grapes.

The ash, according to König, contains—

Per cent. of ash in dry substance		K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	SiO_2	Cl
Whole fruit	3·95	53·0	3·7	6·9	3·3	1·2	21·3	5·0	3·6	1·8
Skin	4·03	44·2	1·9	21·0	5·7	1·5	17·6	3·7	3·0	0·6
Seeds	2·81	28·7	—	33·9	8·6	0·6	24·0	2·5	1·1	0·3

About 0·2 p.c. of manganese oxide is also usually present.

Boric acid bas been found in grapes (Crampton, Amer. Chem. J. 11, 227; Baumert, Ber. 21, 3290). Salicylic acid also occurs, especially in the stalks (Mastbaum, Chem. Zeit. 1903, 27, 829).

Dried grapes constitute raisins and currants and are extensively used. Their average composition, as given by König, is respectively—

	Raisins	Currants
Water	24·5	25·4
Nitrogenous substances	2·4	1·2
Fat	0·6	—
Free acid	1·2	1·5
Invert sugar	59·3	61·8
Cane sugar	2·0	—
Other carbohydrates	1·3	5·9
Crude fibre and seeds	7·0	2·4
Ash	1·7	1·8

American analyses give considerably less water and more ash than these figures.

H. I.

GRAPE FRUIT (*Pomelo*, Shaddock). The fruits of various sub-varieties of *Citrus decumana* (Murr.), indigenous in Java, only some of which are edible. All contain a bitter principle (naringin, *q.v.*), and the non-edible varieties yield the oil of bitter orange or 'neroli-oil' (*see* Orange Flower Oil, Art. Oils, Essential). By steam distillation the rind yields from 1 to 5 p.c. of a clear yellow oil with an odour like citral, $[n]_D$ 20°=1·475–1·4785; optical activity in 100 mm. tube at 20°=+72·5 and +78·5; sp.gr. 0·845–860 at 20°. It contains *d*-limonene, 90–92 p.c.; citral, 3–5 p.c.; *a*-pinene, 0·5–1·5 p.c.; geraniol, 1–2 p.c.; linalool, 1–2 p.c.

Grape fruit is the richest of all the citrus fruits in pectin and pectose materials: the average of recoverable pectin being considerably above 10 p.c. of the peel weight.

GRAPE SEED OIL is obtained from grape seeds (*Vitis vinifera* [Linn.]) by expression or by extraction. As yet the oil is only of local importance, and is expressed only for local consumption, although it has been estimated that the waste seeds from the manufacture of oil in Italy would yield about 18,000 litres of oil per annum. In Italy and in the south of France (and even in south Germany) it is said to be used as an edible oil. The cold-expressed oil has a golden-yellow colour, and is free from odour. If the seeds have been stored for some time the expressed oil is dark, and acquires a slightly bitter flavour. The chemistry of this oil is not fully known, as the *data* obtained by the several observers who examined grape seed oil are very conflicting. At first it was credited with a very high acetyl value, and was compared in this respect with castor oil, so that its use for the manufacture of Turkey red oil had been proposed. More recent examinations have shown that grape-seed oil has a very high iodine value, so that the oil would seem to belong to the semi-drying or drying oils. The discrepancies in the recorded values are probably due to the oils yielded by the seeds of grapes of different varieties differing in their characteristics. For example, a genuine specimen of grape seed oil examined by Paris had an iodine value of 96, and an acetyl value of 143, whereas another oil of undoubted purity examined by dell' Acqua had an iodine value of 143, and an acetyl value of 17·8.

André (Comptes rend. 1921, 172, 1413) separated the hydroxy fatty acids by fractional crystallisation of the lithium salts from dilute alcohol. The average composition of the mixed fatty acids was: solid acids, 12·5, liquid acids, 62·5, and viscous hydroxy acids, 25·0 p.c. The low molec. weight (277) of the hydroxy fatty acids did not support the view that they consisted of ricinoleic acid.

The oil-cake from the expressed seeds is fairly rich in proteins and potassium phosphate. A sample examined by Paris (Staz. sper. Agrar. Ital. 1911, 44, 669) contained 9·12 p.c. of proteins, 4·25 p.c. of fat, and 3·15 p.c. of ash, which contained 14·33 p.c. of phosphoric anhydride and 22·33 p.c. of potassium oxide.

J. L.

GRAPHIC TELLURIUM *v.* Tellurium.

GRAPHITE, a form of carbon crystallised in the rhombohedral system, known also as *plumbago*, and popularly as *black lead*. It occurs usually as compact and crystalline masses, but occasionally as six-sided tabular crystals which cleave into flexible laminæ parallel to the basal plane. It is iron-black or steel-grey in colour, with metallic lustre, and has a sp.gr. of 2·25. In consequence of its softness (H.=1) and the ease with which it produces a metallic streak when rubbed on paper, it is largely used in the manufacture of pencils, whence the name 'graphite' given to it by Werner, from γράφω (I write). It was formerly called *molybdæna*, and confused with molybdenite (MoS_2), a mineral which also gives a metallic mark on paper. (On the history of these names, and of plumbago, *v.* J. W. Evans, Trans. Philological Soc. 1908, 133.) Graphite seems to have been first recognised as a distinct mineral by Gesner, who figured a lead pencil in 1565 (Roscoe). Scheele in 1779 showed that graphite was a kind of mineral carbon, since it could be converted into carbon dioxide by the action of nitric acid. As the carbon is usually associated with more or less iron, the older mineralogists described the mineral as a 'carburet of iron,' but Vanuxem demonstrated that the iron is present as ferric oxide and not as a carbide. The ash left on the combustion of graphite usually contains, in addition to the ferric oxide, silica, alumina, and lime.

Exposed on platinum foil to the flame of the blowpipe, graphite burns, but often with more difficulty than diamond. When heated with a mixture of potassium dichromate and sulphuric acid, it disappears. In order to obtain perfectly pure graphite, the mineral is first ground and washed to remove earthy matter, and then treated, according to Brodie's method, with potassium chlorate and sulphuric acid; on subjecting the resulting product to a red heat, pure carbon is obtained in a remarkably fine state of division.

The following analyses are selected from a large number by C. Mène (Compt. rend. 64, 1091):

	I	II	III	IV
Carbon . .	91·55	81·08	79·40	78·48
Volatile matters	1·10	7·30	5·10	1·82
Ash . .	7·35	11·62	15·50	19·70
	100·00	100·00	100·00	100·00

I. Very fine Cumberland graphite, sp.gr. 2·345. II. Graphite from Passau, Bavaria, sp.gr. 2·303. III. Crystallised graphite, from Ceylon, sp.gr. 2·350. IV. Graphite from Buckingham, Canada, sp.gr. 2·286.

Graphite when used for pencils is frequently mixed, in a powdered state, with pure clay, and the mixture consolidated by hydraulic pressure. It is also sometimes mixed with sulphur or with antimony sulphide. Brockedon first suggested the use of the hydraulic press as a means of obtaining from powdered graphite a homogeneous and coherent mass, which could be readily sawn into pieces of convenient size. The finest pencil lead was yielded by the ancient mine at Borrowdale in Cumberland, where it occurred in pipes, strings, and irregular masses, or 'sops,' associated with a dyke of diorite and with intrusive masses of diabase, in the Cambro-Silurian volcanic series known as 'the green slates and porphyries.' The Cumberland graphite was formerly termed 'wad,' a name sometimes applied also to native oxide of manganese. (For description of the old Borrowdale workings *v.* J. C. Ward in Geol. Survey Mem. on Lake District, 1876.) A small amount of graphite, about 100 tons per annum, is obtained from the Craigman mine, near Cumnock in Ayrshire; here the mineral usually exhibits a columnar structure, and it has been produced by the baking action of dykes of igneous rock on seams of coal (*v.* Special Reports on the Mineral Resources of Great Britain, Mem. Geol. Survey, vol v. 2nd ed. 1917).

Excellent graphite is found in Siberia, especially at the Mariinoskoi mine, in the Tunkinsk Mountains, Government of Irkutsk. This deposit, discovered in 1838, occurs in gneiss, associated with diorite; it has been largely worked by M. Alibert to supply Faber's pencil factory. In 1860 graphite was discovered in granite near the river Nizhne Tungusska, and workings were undertaken by M. Siderov. (For Russian graphite *v.* N. Koksharov, Materialien z. Mineralogie Russlands, 1862, 4, 153, where analyses are given.)

The best quality of graphite found in large quantities is that from Ceylon. The mineral is widely distributed through the western and north-western provinces of the island, and is obtained from a large number of small pits, there being but few mines of any size. The output amounts to about 30,000 tons per annum, with a value of rather over half a million pounds sterling. In 1916 the output was 33,400 tons, valued at £1,500,000, of which 80 p.c. was imported by America. (On the graphite deposits of Ceylon *v.* A. K. Coomaraswamy, Mineralogical Survey of Ceylon, 1903, etc.; Quart. J. Geol. Soc. 1900, 56, 590.) In India, graphite is found at several localities, chiefly in the Madras Presidency, the best coming from Travancore, but even this is far inferior to that from Ceylon.

In the United States, graphite is widely diffused, but rarely in sufficient quantity to be worked. The principal locality is Ticonderoga, in Essex Co., New York, where the Dixon Crucible Co have worked a schist containing about 10 p.c. of graphite. It has also been worked to a limited extent near Raleigh, North Carolina; at Stourbridge, Mass.; at Cumberland Hill in Rhode I.; and at Sonora in California. The graphite 'ores' are crushed or stamped, and then washed, whereby the flakes of graphite are readily separated from the denser matrix. In the Laurentian gneiss of Canada, graphite is of frequent occurrence, and has occasionally been worked, as at the Buckingham Mines. The mineral is usually found in veins and nodular masses, or finely disseminated through bands of limestone. It is widely distributed in the gneissic rocks of Madagascar, and is there mined at a number of localities. In 1917 the French colony exported over 33,000 tons, divided almost equally between France and England. Graphite is also extensively mined at several places in Korea, where the deposits have the form of beds, nests, stocks, and veins in gneiss and metamorphosed Palæozoic sediments.

In Europe, extensive deposits of graphitic schists occur in the Eastern Alps and in the mountainous region between Bohemia and Bavaria (Böhmerwald) These are extensively mined in Moravia, Styria, and particularly in the east of Bohemia, where the annual output reached 50,000 tons; but the material is of inferior quality, containing often 50 p.c. of ash. Considerable amounts are also obtained in the north of Italy, but the well-known locality at Passau in Bavaria is now little worked. (On Alpine Occurrences of Graphite *v.* E. Weinschenk, Abh. bayer. Akad. Wiss. 1898, 19, 509, 521; 1901, 21, 279.)

Daubrée has obtained graphite artificially by decomposing carbon disulphide in contact with metallic iron at a high temperature; while H. Sainte-Claire Deville prepared it by passing vapour of carbon tetrachloride over fused cast iron. Crystalline graphite is often formed in blast furnace slag during iron smelting, and is known to workmen as *kish*; and it is present in grey pig iron. Considerable quantities of graphite are now produced commercially, together with carborundum, in the electric furnace. The artificial production of graphite (as well as various properties of the natural mineral) is dealt with by H. Moissan (The Electric Furnace, London, 1904). Graphite also occurs in certain meteoric irons, such as that of Toluca in Mexico. A cubic form of graphitic carbon, discovered in a meteoric iron from Youndegin, Western Australia, has been described by Fletcher under the name of *Cliftonite* (Min. Mag. 1887, 7, 121).

In consequence of its refractory character, graphite is largely used in the manufacture of crucibles, retorts, twyers, and other objects required to withstand high temperatures. For crucibles, the powdered mineral is mixed with Stourbridge fire-clay, and made into a paste with water; the kneaded mass is allowed to lie for many weeks before the crucible is moulded; the vessel when moulded is slowly dried, and carefully fired in a seggar.

As a lubricating agent graphite is highly valued, since it diminishes friction and tends to keep the moving surfaces cool. To obtain the best results the powdered mineral should be carefully selected and sized. For steam cylinders it is used dry; for heavy bearings it is mixed with grease; and for light bearings with oil. Made into a paint with linseed oil, it has been advantageously employed as a coating for metal work. Graphite is also used dry for polishing stoves and other objects of cast iron, the thin flakes forming a lustrous coating which protects the metal. Blasting powder and heavy ordnance powders are likewise glazed with graphite, for though it slightly diminishes the explosive force of the powder it protects it from damp. Being a good conductor of electricity, graphite is used in electrotyping, as originally suggested by Murray; the moulds upon which the metal is to be deposited receiving a conducting surface by being coated with finely divided graphite.

For the method of rapidly analysing graphite in use at the Pittsburgh Laboratory of the U.S. Bureau of Mines, *see* U.S. Bureau of Mines Bull. 112, 1920, 43; J. Soc. Chem. Ind. abstr. 1920, 70 A.

E. Donath, Der Graphit, eine chemisch-technische Monographie, Leipzig and Wien, 1904; Graphite, its Occurrence and Uses, Bull. Imp. Inst. London, 1906, 4, 353; 1907, 5, 70; F. Cirkel, Graphite, its Properties, Occurrence, Refining, and Uses, Dept. of Mines, Ottawa, 1907, Publ. No. 18; H. S. Spence, Graphite, Dept. of Mines, Ottawa, 1920, Publ. No. 511; A. Haenig, Der Graphit, eine technische Monographie, Wien and Leipzig, 1910; O. Stutzer, Die wichtigsten Lagerstatten der 'Nicht-Erze,' Berlin, 1911. L. J. S.

GRAPHITIC ACID and **GRAPHITIC OXIDE.** Prepared by Balbiano from natural and Acheson graphite varied in composition between $C_{13}H_4O_7$ and $C_{14}H_4O_7$, and on being heated *in vacuô* yield carbon monoxide and dioxide, together with methane and water. They are regarded as absorption compounds of graphite, water, and carbon monoxide and dioxide, and not true chemical compounds as assumed by Brodie (*cf.* Kontschütter and Haenni, Zeitsch. anorg. Chem. 1919, 105, 121).

GRASSES. The term 'grass' is used by the agriculturist to denote, not only plants which belong to the *gramineæ*, but also other pasture or meadow plants, or even certain weeds common on cultivated land.

The true grasses are characterised by a somewhat low content of nitrogenous substances, and by the richness of the ash in silica and its poverty in lime and magnesia, whilst clovers and other leguminous crops possess the exactly opposite features. H. I.

GREASES. The term 'grease' was applied originally to all kinds of fats having a buttery consistence. At present, however, the term 'grease' is restricted to low-class material, chiefly obtained from waste products, such as kitchen grease, ship's grease, tripe tallow, slaughter-house grease ('tankage' grease), bone grease, skin grease, greases from carcase-rendering establishments, and garbage fats. All these greases must be looked upon as varieties and (or) mixtures of lard, tallow, bone fat, horse fat, fish stearines, &c.

Greases are characterised by a dark colour, by a high percentage of free fatty acids, and a correspondingly high proportion of unsaponifiable matter. They have also an objectionable odour.

Black grease is the dark, almost black, fatty matter which is recovered from cotton seed mucilage, on decomposing the latter with mineral acids (*see* COTTON SEED OIL). This black grease is used in the manufacture of low-class candle materials, after a purification by distillation with superheated steam, and further treatment of the distillate in the same manner as in working up the fatty acids in the candle industry (*see* SAPONIFICATION). J. L.

GREEN ALIZARIN *v.* MADDER.

GREEN CINNABAR. A mixture of chrome yellow and Prussian blue.

GREEN EBONY. Green ebony is a yellow dyewood formerly employed to some extent in this country, but is now almost entirely replaced by other colouring matters. It is a native of Jamaica or West India, and is obtained from the *Excœcaria glandulosa* (Siv.) or *Jacaranda ovalifolia* (R. Br.). The trunk of the tree is about 6 inches in diameter; the wood is very hard, and of an orange-brown colour when freshly cut, and stains the hands yellow. References to this dyestuff are meagre, and it does not appear to have been ever largely employed. Bancroft (Philosophy of Permanent Colours, 1813, ii. 106) states that green ebony contains a species of colouring matter very similar to that of the *Chlorophora tinctoria* (Gaudich) (Old fustic), and is sometimes employed in its stead; and O'Neill (Dictionary of Calico Printing and Dyeing, 1862) mentions that it is used in dyeing greens and other compound shades. Until recently it had a limited sale in Yorkshire as a dye for leather, but appears to have entirely passed out of use as a woollen dyestuff. It is now little used in silk dyeing, but was formerly employed for greening blacks.

Green ebony contains two crystalline colouring matters, which are distinguished by the fact that whereas one, excœcarin, is not precipitated by lead acetate solution, the second, jacarandin, is completely deposited by this reagent (Perkin and Briggs, Chem. Soc. Trans. 1902, 81, 210).

Excœcarin $C_{18}H_{12}O_5$, crystallises in lemon-yellow needles, sparingly soluble in cold alcohol, and melting with effervescence at 219°–221°. It is soluble in aqueous and alcoholic alkaline solutions with a violet-red coloration, and these liquids, on exposure to air, are rapidly oxidised, and assume a brown tint.

Excœcarin does not dye mordanted fabrics, but is a substantive dyestuff in that it has a weak but decided affinity for the animal fibres with which it gives, preferably in the presence of tartaric or oxalic acid, yellow shades. *Benzoylexcœcarin* $C_{18}H_9O_5(C_7H_5O)_3$, consists of colourless needles, m.p. 168°–171°, and *excœcarindimethyl ether*, $C_{18}H_{10}O_5(CH_3)_2$, of yellow needles, m.p. 117°–119°. On fusion with alkali excœcarin gives *hydroquinonecarboxylic acid*

$$(CO_2H : OH : OH = 1 : 2 : 5)$$

and a substance melting at 124°, which is probably *hydrotoluquinone*

$$(CH_3 : OH : OH = 1 : 2 : 5)$$

By the action of bromine upon a solution of excœcarin in alcoholic potassium acetate *excœcarone* $C_{13}H_{10}O_5$, flat copper-coloured needles or leaflets, melting at about 250°, is produced, and this by the action of sulphurous acid is reconverted into excœcarin. With alcoholic quinone solution excœcarin gives the compound $C_6H_4O_2 \cdot C_{13}H_{12}O_5$, minute green-coloured leaflets, melting with decomposition at 190°, and from this sulphurous acid also regenerates excœcarin. From these results it appears evident that excœcarin contains free hydroquinone hydroxyls.

Jacarandin $C_{14}H_{12}O_5$, yellow plates or leaflets, m.p. 243°–245°, dissolves sparingly in alcohol and the usual solvents to form pale yellow liquids having a green fluorescence. With caustic alkali solutions it gives orange-red liquids; with alcoholic lead acetate a bright orange-coloured precipitate; and with alcoholic ferric chloride a dark greenish-black solution. It dyes mordanted woollen fabrics the following shades:

Chromium	*Aluminium*	*Tin*	*Iron*
Dull yellow-brown	Orange-brown	Bright golden yellow	Deep olive

Acetyljacarandin $C_{14}H_{10}O_5(C_2H_3O)_2$, pale-yellow needles, melts at 192°–194°, and when digested with boiling alcoholic potassium acetate gives the salt $(C_{14}H_{12}O_5 \cdot C_{14}H_{11}O_5)K$, yellow needles. *Benzoyljacarandin* $C_{14}H_{10}O_5(C_7H_5O)_2$, forms yellow prismatic needles, m p. 167°–169°.

As indicated by Bancroft (*l.c.*) the colours given by green ebony are similar in character to those yielded by old fustic. Employing mordanted woollen cloth the following shades are produced:

Chromium	*Aluminium*	*Tin*	*Copper*	*Iron*
Dull yellow-brown	Dull brown-yellow	Golden yellow	Pale brown	Olive green

With 40 p.c. of the dyewood the iron mordant gives greener and brighter shades than with larger amounts, in which case a browner colour is produced. Possibly from this green shade, and the extremely hard and compact nature of the wood, the name 'green ebony' has originated.

A. G. P.

GREEN, EMERALD, *v.* Chromium.

GREEN, GUIGNET'S, *v.* Chromium.

GREEN SMALT, *Cobalt green*, *v.* Pigments.

GREEN ULTRAMARINE, *Chromium sesquioxide*, *v.* Chromium.

GREEN VITRIOL, *Ferrous sulphate*, *v.* Iron.

GREENALITE. A hydrated iron silicate ccurring in the form of green granules in sedimentary rocks, and closely resembling glauconite (q.v.), from which it differs in containing no otassium. The composition varies somewhat; ne analysis gives the formula

$$Fe_2''(Fe'',Mg)_3(SiO_4)_3 \cdot 3H_2O$$

t occurs abundantly on the Mesabi Range in he Lake Superior district of Minnesota, and y its alteration has given rise to ferruginous herts and immense deposits of iron ore (C. K. eith, Monograph U.S. Geol. Survey, 1903, liii.).

L. J. S.

GREEN-EARTH. (Ger. *Grünerde*). A term oosely applied to a variety of earthy minerals f a bluish-green, or dark olive-green colour occurring as alteration products in basic igneous rocks. It includes more particularly the species *celadonite* (or seladonite), and various indefinite members of the chlorite group, *e.g.* delessite, chlorophæite, kirwanite, viridite, &c. Many of these are of indefinite composition and probably mixtures. They are often met with as a green lining in the amygdaloidal cavities of altered basaltic rocks, and form the 'skin' of agates and other secondary minerals filling these cavities. Crystals of augite in the same rocks are sometimes completely altered to a soft aggregate of green-earth still preserving the sharp outlines of the original crystals. Similar pseudomorphs after hornblende also occur. Larger irregular masses fill cavities and fissures in these rocks. The well-known green-earth of Monte Baldo near Verona is referable to celadonite. An analysis of material from this locality gave: SiO_2, 54·84; TiO_2, 0·10; Al_2O_3, 1·22; Fe_2O_3, 19·16; FeO, 4·39; MnO, 0·28; CaO, 0·24; MgO, 5·34; K_2O, 9·75; Na_2O, 0·82; H_2O, 3·77=99·9 (C. W. Gümbel, 1896). This composition is very similar to that of glauconite, with which celadonite is perhaps identical, differing only in its state of aggregation and mode of origin and occurrence. This celadonite green-earth is worked commercially as a pigment on both sides of the Tyrolese-Italian border; and similar material could be obtained from many other localities.

L. J. S.

GREENLAND SPAR *v.* Cryloite.

GREENOCKITE. Cadmium sulphide CdS, crystallised in the hexagonal system with hemimorphic development and isomorphous with wurtzite (ZnS). This and the still rarer cadmium oxide, and otavite (basic carbonate), are the only minerals that contain cadmium as an essential constituent. Distinct, though small, crystals are found only in Scotland, in the neighbourhood of Glasgow. They occur very sparingly with prehnite in amygdaloidal basalt in the Bishopton railway-tunnel and the Boylestone quarry at Barrhead in Renfrewshire, and in the Bowling quarry in Dumbartonshire. They are honey- to orange-yellow, transparent to translucent, and have a resinous to adamantine lustre; the streak is orange- to reddish-yellow. Sp.gr. 4·8–4·9; H. 3–3½. Traces of cadmium are often present in zinc-blende (up to 1·5 p.c., and in the ores of the Joplin district in Missouri averaging 0·358 p.c.), and with the weathering of this mineral cadmium sulphide remains as a thin, powdery, canary-yellow coating ('cadmium-ochre'), or it may impart a tinge of colour to the secondary zinc minerals hemimorphite and smithsonite ('turkey-fat ore'). In this form the mineral is known from many localities, though never in large amount. Being colloidal, it does not agree with the definition of greenockite as given above; and, again, the possible existence of a cubic form of cadmium sulphide is suggested by the isomorphous presence of this constituent in zinc-blende, although this modification has not been prepared artificially The new name xanthochroite (A. F. Rogers, 1917) has therefore been suggested for this colloidal form of cadmium sulphide. Hemimorphic hexagonal crystals of cadmium sulphide have been prepared artificially, and they are not uncommon as furnace products. The artificial crystals have sp.gr. 4·820 and the high refractive indices ϵ_{Na} 2·529, ω_{Na} 2·506.

L. J. S.

GREENSAND *v.* Glauconite.

GREENSTONE *v.* Diabase and Jade.

GRENAT BROWN *v. iso*-Purpuric acid.

GREY ANTIMONY ORE, *Antimony sulphide, v.* Antimony.

GREY OIL. A mixture of lanoline vaseline, and metallic mercury. Used in the treatment of syphilis.

GRIFA. Trade name for lithium acetylsalicylate.

GRIGNARD REAGENT. Grignard, in 1901, showed that magnesium reacts with alkyl and aryl halides in presence of ether at ordinary temperatures forming compounds of the type R.Mg.X (where R is an aryl or alkyl radicle and X a halogen radicle) which are synthetic reagents of great value and capable of extensive application.

For a discussion of the probable constitution of these magnesium compounds, *see* Meisenheimer and Casper, Ber. 1921, 54 [B], 1665. Chem. Soc. Abstr. 1921, i., 654.

GRINDELIA. (B.P.) The dried leaves and flowering tops of *Grindelia camporum* (Greene).

GRISERIN. Trade name for the sodium salt of iodo-hydroxy-quinoline-sulphonic acid. Used in treatment of tuberculosis.

GRI-SHI-BU-ICHI. Japanese name for an alloy of copper and silver of a rich grey colour.

GRISOUTINE. An explosive consisting of a mixture of nitroglycerin, nitrocellulose, ammonium nitrate, and kieselguhr.

GROSSULARITE *v.* Garnet.

GROTAN. A chlorinated cresol used as a bactericide.

GRÜNLINGITE *v.* Tetradymite.

GUACAMPHOL, CUAIACETIN, GUAIAFORM, GUAIAKINOL, GUAIAMAR, GUAIASANOL, GUATANNIN *v.* Synthetic drugs.

GUAICHINOL. Trade name for quinine dibromoguaicolate.

GUAIACENE *v. Guaiacum,* art. Resins.

GUAIACIC ACID *v. Guaiacum,* art. Resins.

GUAIACOL (*Monomethoxycatechol*)

$$OH\cdot C_6H_4\cdot OMe$$

is a constituent of guaiacum resin (Herzig and Schiff, Monatsh. 1898, 19, 95), and occurs in beechwood tar, from which it can be separated by treating the fraction of the tar that comes over at 200°–205° with ammonia to remove acids; it is then again fractionated, and the lower boiling fraction is dissolved in ether and treated with potassium hydroxide. The potassium salt of guaiacol is filtered, washed with ether, and recrystallised from alcohol, after which it is decomposed with sulphuric acid, and the guaiacol redistilled. (For other methods of separation, *cf.* D. R. PP. 87971, 56003, 100418, Chem. Zentr. 1899, i. 764.) Guaiacol is prepared from *o*-anisidine. 500 grams *o*-anisidine are diazotised, and the solution of the diazo salt is then poured into a boiling solution of 600 grams of copper sulphate in 600 c.c. of water. The guaiacol is then separated by distillation in steam (D. R. P. 167211; Frdl. 1905–7, 128; *cf.* also D. R. P. 95339; J. Soc. Chem. Ind. 1898, 269, 314).

Pure guaiacol can be obtained by dissolving catechol (55 parts) in ethyl alcohol (2000 parts) and adding nitrosomonomethyl urea. The mixture is cooled to 0° and 20 parts of sodium hydroxide dissolved in a small quantity of water is added, drop by drop, with constant stirring. The solution is filtered, the alcohol distilled off, and the residue is fractionated *in vacuô* (D. R. P. 189843; Frdl. 1905–7, 1151).

Guaiacol is also prepared by heating an equimolecular mixture of catechol, potash, and potassium methyl sulphate in tightly closed vessels at 170°–180°, or by heating catechol and methyl iodide in methyl alcohol. A weak base, such as sodium carbonate or sodium hydrogen carbonate, is gradually added to a mixture of catechol, with the alkali or alkali earth salts of methylsulphuric acid in the presence of veratrole as diluent at 160°–180° (Zollinger and Röhling, D. R. P. 305281; Chem. Soc. Abst. 1918, i. 497). Thompson (Eng. Pat. 5284, 1893) suggests the purification of guaiacol by treatment with a freezing mixture.

Guaiacol has a characteristic odour and crystallises in long vitreous transparent prisms, which appear rose-red in sunlight; m.p. 28·5°, b.p. 202·4°/738 mm. (Freyss, Chem. Zeit. 1894, 18, 565); sp.gr. 1·140 at 25°. When quite pure it is non-caustic and non-poisonous (Béhal and Choay, Compt. rend. 1893, 116, 197; Kuprianow, J. Soc. Chem. Ind. 1895, 57).

It is soluble in most organic solvents, and to a less extent in water. With a trace of ferric chloride its alcoholic solution gives a blue colour, which becomes emerald-green on the addition of more ferric chloride. Guaiacol also gives a blue colour with traces of hydrogen peroxide (Denigès, J. Pharm. Chim. 1901, 31).

Guaiacol is employed in pharmacy as an expectorant and intestinal antiseptic; also in pulmonary tuberculosis in cases of typhoid and other fevers, and for the relief of superficial neuralgia.

Kuprianow (Centralbl. f. Bakteriol. 1894, 15, 933, 981) has suggested the use of pure guaiacol in the internal treatment of cholera, since he found that a solution of 1 in 500 of this reagent completely prevents the development of the cholera bacillus.

Guaiacol should be preserved in amber-coloured bottles protected from the light, and should only be used in pharmacy when quite pure.

Tests.—(1) 2 c.c. of guaiacol mixed with 4 c.c. of light petroleum, should separate at once into 2 layers. (2) 1 c.c. of guaiacol should dissolve in 2 c.c. of N. sodium hydroxide when heated; on cooling the mixture should congeal to a white saline mass, which gives a clear solution with 20 c.c. of water. (3) 1 c.c. of guaiacol treated with 10 c.c. of N. sulphuric acid should give a pure yellow colour. For other tests, *v.* Marfori, J. Soc. Chem. Ind. 1891, 487; Fonzes Diacon, Bull. Soc. chim. 1898, 19, 191; Guérin, J. Pharm. Chim. 1903, [vii.] 17, 173.

Guaiacol can be estimated approximately by conversion into catechol, by heating with water in a current of hydrobromic acid; or 0·5 gram of the guaiacol is dissolved in a little water, 10 c.c. of alcohol added, and the solution made up to 1000 c.c., and 20 c.c. of this solution are mixed in a test-tube with 1 c.c. of sodium nitrite solution (1 : 100), and 1 c.c. dilute nitric acid (1 : 200). A characteristic red-brown colour is produced, which is compared within about 10 minutes with the colorations given by suitable standard solutions (Adrian, Zeitsch. anal. Chem. 1901, 40, 624).

Guaiacol, when treated with hydrogen cyanide, in the presence of sodium or zinc chloride, yields vanillin (Roesler, D. R. P. 189037; Frdl. 1905–7, 1280; Guyot and Gry, Compt. rend. 1909, 149, 928; Bull. Soc. chim. 1910 [iv.] 7, 902).

Guaiacol monosulphonic acids can be obtained by treating guaiacol with sulphuric acid at 30°–60°, the ortho- and para- acids formed being separated by converting them into the basic salts of the alkaline earths, or of the heavy metals, the ortho- salts being readily soluble in water, whereas the para- salts are insoluble or sparingly soluble. By the action of sulphuretted hydrogen, or some suitable acid, the salts are then converted into their respective acids (D. R. P. 188506; Frdl. 1905–7, 936; D. R. P. 132607; Frdl. 1900–02, 1113; Hähle, J. pr. Chem. 1902, [ii.] 65, 95; Lamière and Perrin, Bull. Soc. chim. 1903 [iii.] 29, 1228; Rising, Ber. 1906, 39, 3685; Paul, *ibid.* 2773, 4093; Ginhorn, Fr. Pat. 391601, 1908; J. Soc. Chem. Ind. 1908, 1176; André, J. Pharm. Chim. 1898, 7, 324).

The most striking difference between the ortho- and the para- acids is their action with calcium or barium chloride, with which the para- acid yields a white precipitate, whereas the torho- remains unchanged. With nitric acid the para- acid forms yellow dinitroguaiacol (m.p. 122°), whilst the ortho- acid merely gives a dark red coloration. It is important that when the ortho- acid is used therapeutically, it should be free from the para- compound, as the latter gives rise to secondary reactions (Ellis, J. Soc. Chem. Ind. 1906, 335).

The alkali guaiacol sulphonates are employed as drugs (Alpers, U.S. Pat. 692588; J. Soc. Chem. Ind. 1902, 364). Tagliavini has prepared salts of the sulphonates with antipyretic and analgesic bases (Boll. Chim. farm. 1909, 48, 6).

Carbonyl chloride condenses with the alkali guaiacol sulphonates in alkaline solutions, giving derivatives such as *potassium carbonatodiguaiacol disulphonate* $CO[OC_6H_3(OMe)SO_3K]_2$, and *potassium carbonatodiguaiacol sulphonate*

$$C_6H_4(OMe)O{\cdot}CO_2C_6H_3(OMe)SO_3K$$

(Einhorn, D. R. P. 203754, 1909).

Guaiacol 5-sulphonic acid is obtained by sulphonating an acetyl derivative of guaiacol with or without the addition of dehydrating agents, tbe resulting acetyl guaiacol sulphonic acid is hydrolysed, neutralised, and the resulting acid is isolated as such, or in the form of its salts (D. R. P. 212389; J. Soc. Chem. Ind. 1909, 1005). The corresponding *carbonate*

$$(MeO{\cdot}C_6H_3SO_3H)_2CO_3$$

is formed by treating guaiacol carbonate with sulphuric acid in the cold until the product is soluble in water. It melts at 115°–117°, with evolution of carbon dioxide (D. R. P. 215050; J. Soc. Chem. Ind. 1909, 1223).

Triphenyl guanidine guaiacol sulphonate is obtained by the action of triphenyl guanidine sulphate on barium guaiacol sulphonate. It crystallises in leaflets, m.p. 50°, and can be used a a local anæsthetic (Goldschmidt, Chem. Zeit. 1901, 25, 628).

A number of important compounds of *o*-guaiacol sulphonic acids with alkaloids are described by Schaefer (J. Soc. Chem. Ind. 1910, 928). They are used in medicine and are also of scientific interest. The alkaloid salts are prepared by neutralising the guaiacol sulphonic acid with the required alkaloid, and purifying the product by filtration and recrystallisation, or the amorphous salt is obtained by evaporation at low temperature or *in vacuó*. The salts may also be obtained by double decomposition between a soluble alkaloid, and a readily soluble salt of the acid in molecular proportions, using alcohol, water, &c., as a solvent. Most of the alkaloid salts are non-crystalline or crystallise with difficulty. The most important of the salts described by Schaefer are:

Quinine guaiacol bisulphonate (guaiaquin) $[C_6H_3(OH)(OMe)SO_3H]_2,C_{20}H_{24}N_2O_2$ is a yellowish crystalline powder, soluble in water, alcohol, and dilute acids. The solution is coloured blue by a drop of ferric chloride solution. It softens at about 80°, and becomes liquid at 130°.

Codeine-o-guaiacol sulphonate

$$C_6H_3(OH)(OMe)SO_3H,C_{18}H_{21}NO_3$$

m.p. 164°–165°, is a well-crystallised neutral salt. It is readily soluble in hot water and in alcohol, but almost insoluble in ether and chloroform. It gives the characteristic blue coloration of *o*-guaiacol sulphonic acid with ferric chloride, and when its aqueous solution is treated with an alkali, codeine is precipitated. Other opium and cinchona compounds, as well as compounds with strychnine, brucine, atropine, hyoscine, hyoscyamine, and cocaine, are described.

Guaiacol iron and lithium sulphonates have been prepared (Schaefer, Eng. Pat. 21747, 1899).

Guaiakinol, quinine derivative of bromo-guaiacol, $C_{20}H_{24}N_2O_2,2HBr,C_6H_4(OH)(OMe)$, forms fine crystalline yellow scales, readily soluble in water. It is said to be practically non-toxic, and its aqueous or alcoholic solution is readily absorbed by the skin (Pharm. J. 1901, 66, 132; Schaefer, Eng. Pat. 8227, 1897).

Guacamphol, the camphoric acid ester of guaiacol $C_8H_{14}(CO{\cdot}OC_6H_4{\cdot}OMe)_2$, obtained by the action of camphoric acid chloride on sodium derivative of guaiacol. Forms white, odourless, tasteless needles, and has been recommended for the relief of night sweats in phthisis.

Guaiacol benzoate (benzosol, benzoyl guaiacol) $C_6H_5{\cdot}CO{\cdot}OC_6H_4{\cdot}OMe$ is prepared by heating an alcoholic solution of potassium derivative of guaiacol with the requisite amount of benzoyl chloride, and purifying the substance by crystallisation from alcohol. It is a colourless, odourless, tasteless powder, almost insoluble in water, readily soluble in organic solvents. It has m.p. 56°, and is used in the treatment of pulmonary tuberculosis (Eng. Pat. 5366, 1890; J. Soc. Chem. Ind. 1891, 383; Walzer, Chem. Zeit. Rep. 1891, 15, 165).

Guaiacol cinnamate (styracol, cinnamyl guaiacol) $C_8H_7{\cdot}CO{\cdot}OC_6H_4{\cdot}OMe$ is formed by the interaction of molecular weights of guaiacol and cinnamyl chloride. It forms colourless needle-shaped crystals, m.p. 130°, which are employed in catarrhal affections of the digestive tracts, and in the treatment of phthisis.

Guaiacol combines with tannin and cinnamic acid to form a compound which is said to be of use in medicine. It melts above 300°, is insoluble in most organic solvents, and dissolves in alkalis and also in pyridine, from which the pyridine derivative crystallises in well-shaped rhombic needles (D. R. P. 133299; Frdl. Nissel. 1900–02, 1111).

Guaiacol valerate $C_4H_9{\cdot}CO{\cdot}OC_6H_4{\cdot}OMe$, a yellowish oily liquid, b.p. 245°–265°, is used in medicine under the name of *geosote* (Rieck, J. Soc. Chem. Ind. 1897, 632). It is prepared by the action of valeryl chloride on sodium derivative of guaiacol.

Guaiacol salicylate (guaiacol salol)

$$C_6H_4(OH)CO{\cdot}OC_6H_4{\cdot}OMe$$

is a white crystalline, odourless, tasteless powder; m.p. 65°. It is formed by the action of phosphorus oxychloride on a mixture of sodium guaiacol salicylate, and is used as an intestinal antiseptic.

Guaiacol succinate $C_2H_4(CO{\cdot}OC_6H_4{\cdot}OMe)_2$ is formed by the action of phosphorus oxychloride on a mixture of guaiacol and succinic acid in molecular proportions. It forms fine silken crystalline needles; m.p. 136°.

Guaiamar, the *glyceryl ether of guaiacol* $C_6H_4(OMe)OC_3H_7O_2$, is formed by the action of anhydrous glycerol on guaiacol. It is a white crystalline body, m.p. 75°, soluble in water and in most organic solvents. It has a bitter aromatic taste, and is employed in medicine as an antiseptic for internal and external application (J. Soc. Chem. Ind. 1900, 371; 1902, 1346).

Guaiasanol (diethylglycocollguaiacol hydrochloride) $MeO,C_6H_4O{\cdot}CO{\cdot}CH_2NEt_2,HCl$, m.p. 184°, is non-poisonous, and said to possess slight anæsthetic, antiseptic, and deodorising properties (Einhorn, Chem. Zeit. Rep. 1900, 24, 33; J. Soc. Chem. Ind. 1900, 464). By the action of the monochloracetic esters of phenols with secondary amines of the fatty series, many compounds, similar to the above, have been prepared (Einhorn and Heinz, Arch. Pharm. 240 [8] 631; D. R. P. 105346). They are non-poisonous, odourless, and strongly antiseptic substances.

Guaiaperol (piperidine derivative of guaiacol) is prepared by dissolving 85 parts of piperidine and 248 parts of guaiacol in benzene or light petroleum, and allowing the solution to evaporate (Tunnicliffe, Chem. Soc. Trans. 1898, 145).

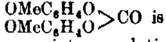
Valuable albuminous products said to be applicable in medicine for tuberculous and other cases are obtained by the interaction of guaiacol with egg or other albumin in aqueous or alcoholic solution (D. R. P. 162656; Frdl. 1905–7, 931).

Guaiacol, when treated with ethoxyacetyl chloride, bromide, or iodide, reacts thus:

$$MeO{\cdot}C_6H_4{\cdot}O|H+Cl|COCH_2OEt \rightarrow MeO{\cdot}C_6H_4CO{\cdot}OCH_2OEt.$$

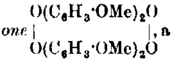
The product is a colourless, odourless oil; b.p. 150°/10 mm. The corresponding methoxy derivative boils at 170°–171°/10 mm., and has very similar properties to the ethoxy derivative. Both substances are non-poisonous, and can be used therapeutically as external remedies (D. R. P. 171790; Frdl. 1905–7, 933).

Guaiaform (geoform) is produced by the condensation of guaiacol (2 mols.) with formaldehyde (1 mol.). It is a tasteless, yellow, non-irritant, and non-toxic powder, but on keeping it acquires the vanilla flavour. It is insoluble in water, but readily soluble in ether, benzene, or alcohol (Ehlert, Pharm. J. 1902, 68, 61).

Guaiacol carbonate  $\begin{matrix}OMeC_6H_4O\\OMeC_6H_4O\end{matrix}>CO$ is prepared by passing phosgene into a solution of guaiacol in sodium hydroxide. The substance is filtered off, washed with sodium hydroxide solution, and recrystallised from alcohol. It is a white crystalline powder, m.p. 84°–87°, of neutral reaction, and almost odourless and tasteless, soluble in most organic solvents, but insoluble in water. Its alcoholic solution yields no characteristic colour with ferric chloride. When taken internally its action is very similar to that of guaiacol, but it is less liable to derange the stomach. It is employed as an expectorant in the treatment of tuberculosis and bronchitis, and also as an intestinal antiseptic in the treatment of typhoid fever and intestinal indigestion (D. R. PP. 99057, 58129, 117346, of 1901; D. R. P. 224160; Einhorn, Chem. Zentr. 1910, ii. 518).

Guaiacol chlorocarbonate is a colourless oil; b.p. 112°/25 mm. It is prepared by the interaction of antipyrine, carbonyl chloride, and guaiacol (D. R. P. 117624 of 1901; Einhorn, D. R. P. 224108, 1910; Chem. Zentr. 1910, ii. 517).

Guaiacol carboxylic acid $C_6H_3(OH)(OMe)CO_2H$ is formed by the action of carbon dioxide on sodium derivative of guaiacol, previously heated; the product is heated for some time, and is then acidified with hydrochloric acid, the free acid being recrystallised from water or dilute alcohol. It is a white, odourless crystalline powder; m.p. 148°–150°. It has a bitter taste, is readily soluble in hot water, and its aqueous solution is coloured blue by ferric chloride. The acid and its salts have been recommended as antiseptics and antirheumatics (Pharm. J. 1890, 977).

Guaiacol, when oxidised with laccase, yields *tetraguaiacoquinone*  $\begin{array}{|c|}O(C_6H_3{\cdot}OMe)_2O\\ \\ O(C_6H_3{\cdot}OMe)_2O\end{array}$, a fine crystalline powder, m.p. 135°–140°, having a purplish-red colour with a faint green metallic lustre. It is insoluble in water, but gives mahogany-red solutions with chloroform and with acetic acid. It also forms coloured solutions in alkalis (Bertrand, Compt. rend. 1903, 137, 1269).

Dimethylamino ε-guaiacylamyl ether, the corresponding piperido derivative and the piperido-γ-guaiacyl-propyl ether are formed by the interaction of a halogen hydrocarbon alkyl ether of guaiacol with a secondary amine, thus:

$$x(CH_2)_nO{\cdot}R+NHMe_2=Me_2N(CH_2)_nOR; \text{ or}$$
$$x(CH_2)_nO{\cdot}R+NHC_5H_{10}=C_5H_{10}N(CH_2)_nO{\cdot}R$$

(where x=halogen). They are employed in medicine as anæsthetics (D. R. P. 184986; Frdl. 1905–7, 1050).

Hexamethylenetetraminetriguaiacol crystallises in brilliant needles, which become soft at 80°, and melt to a turbid liquid at about 95°. When distilled in steam it yields guaiacol (Eng. Pat. 24072, 1908; J. Soc. Chem. Ind. 1909, 490).

Chloroacetyl guaiacol $OMeC_6H_4O{\cdot}CO{\cdot}CH_2Cl$ is prepared by treating a mixture of guaiacol monochloroacetic acid and pyridine with phosphorus oxychloride. It forms white needles, m.p. 58°–60° (Einhorn and Hentz, *l.c.*).

Guaiacol chloroformic ester is a colourless oil; b.p. 112°/25 mm. (D. R. P. 117624; Frdl. 1900–02, 1165).

Benzyl guaiacol is a yellow, beautifully fluorescent oil; b.p. 269°–270°/430 mm. (Boscogrande, Chem. Zentr. 1898, i. 207).

Guaiacol picrate forms orange-red needles; m.p. 80°. Many other guaiacol derivatives have been prepared, some of which have been recommended for use in medicine (Eng. Pat. 5856, 1894; Ruhemann, Chem. Soc. Trans. 1902, 421; D. R. P. 120558; Frdl. 1900–02, 1112; D. R. P. 157355; Frdl. 1902–04, 616; Knapp and Suter, Chem. Zentr. 1904, i. 391; Moureu and Lazennec, Compt. rend. 1906, 142, 894; Bischoff, Ber. 1906, 39, 3846; Gattermann, Annalen, 1907, 357, 313; Fourneau, J. Pharm. Chim. 1910, [vii.] 1, 55, 97; Manchot, Ber. 1910, 43, 949; Wohl and Berthold, *ibid.* 2175; Hoffmann, D. R. P. 255924; Chem. Zentr. 1910, ii. 1105).

A number of azo derivatives of guaiacol are described by Leonardi (Atti R. Accad. Lincei. 1907 [v.] 16, ii. 639); some nitro and amino derivatives by Reverdin and Crepieux, Ber. 1903, 36, 2257; 1906, 39, 4232; Paul, *ibid.* 2773; Kuhling, *ibid.* 1905, 38, 3007; Fichter and Schwab, *ibid.* 1906, 39, 3339; Pollecoff and Robinson, Chem. Soc. Trans. 1918, 113, 645.

Thioguaiacol and *thioguaiacol xanthate* have been prepared by Mauthner (Ber. 1906, 39, 1347).

Guaiacol forms mono-, di-, tri-, and tetrahalogen derivatives (Cousin, Compt. rend. 1898, 127, 759; Tassily and Lerride, *ibid.* 1907, 144, 757; Bull. Soc. chim. 1908, [iv.] 3, 124; Mameli Gazz. chim. ital. 1907, 37, ii. 366; Robertson, Chem. Soc. Trans. 1908, 791). The iodo derivatives are said to be applicable to medicine (Mameli and Pinna, Chem. Zentr. 1907, ii. 2044).

Guaiacol phosphite, m.p. 75·5°, is a white crystalline powder, with a piquant non-caustic taste and slight odour, soluble in most organic solvents, but only sparingly in water (Bollard, D. R. P. 95578; J. Soc. Chem. Ind. 1897, 632; Ellis, Eng. Pat. 27527, 1896). Its medicinal properties are similar to those of guaiacol.

Another *guaiacol phosphite*, m.p. 59°, is described by Dupuis (Compt. rend. 1910, 150, 622).

Guaiacol phosphate $(C_6H_4OMe)_3PO_4$ is prepared by the interaction of phosphorus oxychloride and sodium derivative of guaiacol. It forms colourless crystals; m.p. 98°, insoluble in water and alcohol, but soluble in ether, chloroform, and acetone. It is used as an intestinal antiseptic and in hectic fever.

A number of other phosphorus compounds of guaiacol are described by Auger and Dupuis (Compt. rend. 1908, 146, 1151), and by Dupuis (*ibid.* 1910, 150, 622).

Guaiacol-cacodylate $AsMe_2O_2\cdot C_6H_4OMe$ is a white hygroscopic, crystalline, very unstable salt (Astruc and Murco, J. Pharm. Chim. 12, 553).

GUAIACONE *v. Guaiacum*, art. Resins.

GUAIACONIC ACID *v. Guaiacum*, art. Resins.

GUAIACUM *v.* Resins.

GUAIAMALTIN. Trade name for a mixture of potassium sulpho-guaiacolate and malt extract.

GUAIAPEROL. An addition product of guaiacol and piperidine $C_5H_{11}N(C_7H_8O_2)_2$.

GUAIARETIC ACID $C_{22}H_{24}O_4$ an optically active unsaturated acid, related to eugenol, contained in guaiacum resin and resins.

GUAIATHOL. A condensation product of catechol and ethyl alcohol $C_6H_4OC_2H_5\cdot OH$.

GUAIENE 2·3-dimethyl naphthalene, obtained by dry distillation of guaiacum resin. *v. Guaiacum*, art. Resins.

GUAIOL *v. Guaiacum*, art. Resins.

GUANIDINE $HN:C(NH_2)_2$ occurs in small quantities in etiolated vetch seedlings, 3 kilos. of dried material yielding 1 gram of the nitrate (Schulze, Ber. 1892, 25, 658); in beet juice (Lippmann, *ibid.* 1896, 29, 2651; in *Boletus Edulis* (Winterstein, Landw. Vers.-Stat. 79, 80, 541); and in the developing embryo chick (Burns, Bio-Chem. J. 1916, 10, 263). Guanidine and methyl guanidine are found in the blood and urine in cases of tetania parathyreopriva (Burns and Sharpe, Quart. J. Esp. Physiol. 1917, 10, 203).

Guanidine was first prepared by Strecker (Annalen, 1861, 118, 159) by oxidising guanine with potassium chlorate and hydrochloric acid; and it is obtained in small quantity by oxidising egg albumen with potassium permanganate, or gelatin with barium or calcium permanganate (Lossen, J. Pharm. Chim. [iii.] 31, 32; Kutscher and Kickgraf, Sitzungsber. K. Akad. Wiss. Berlin, 1903, 28, 624); it is formed synthetically (1) by heating biuret and hydrogen chloride at 160°–170° (Finckh, Annalen, 1862, 124, 332); (2) from chloropicrin and alcoholic ammonia at 100° (Hofmann, Ber. 1868, 1, 145); (3) from ethyl orthocarbonate and aqueous ammonia at 150° (Hofmann, Annalen, 1866, 139, 111); (4) from carbonyl chloride and ammonia (Bouchardt, Zeitsch. Chem. 1870, 58); (5) from ammonium chloride and alcoholic cyanamide at 100° (Erlenmeyer, Annalen, 1868, 146, 259); (6) from cyanogen iodide and alcoholic ammonia at 100° (Bannow, Ber. 1871, 4, 161); (7) by the action of *aqua regia* on dicyanodiamide, when a quantitative yield of the nitrate is obtained (Ulpiani, D. R. P. 209431); reduction of tetranitro methane yields guanidine hydrochloride (Rakshit, J. Amer. Chem. Soc. 1914, 36, 1221; *see also* Stähler, Ber. 1914, 47, 909).

Guanidine is usually prepared by heating ammonium thiocyanate for 20 hours at 180°–190°, treating the fused mass with water and allowing the guanidine thiocyanate to crystallise from the solution; it is then purified by animal charcoal and recrystallised from alcohol and water. The thiocyanate is converted into the carbonate by treating the concentrated aqueous solution with one equivalent of potassium carbonate, the solution is evaporated and the residue extracted with hot alcohol in which the guanidine carbonate is insoluble, and this is afterwards recrystallised from water (Delitsch, J. pr. Chem. 1871, [ii.] 9, 2; Volhard, *ibid.* 15; Krall, Chem. Soc. Trans. 1913, 103, 1378; Sharpe, J. Biol. Chem. 1917, 28, 399). According to Goldberg, Siepermann, and Flemming (D. R. P. 1898, 97820), a better yield of guanidine salts is obtained when the ammonium thiocyanate is mixed with wood charcoal and the oxide or salt of a heavy metal, and the mixture heated in a current of ammonia

(1) $2NH_4CNS+ZnO$
$=CH_5N_3,HCNS+ZnS=H_2O$;
(2) $2NH_4CNS+ZnO+PbCl_2$
$=2NH_3+2CH_5N_3,HCl+ZnS+PbS+H_2O$;
or guanidine thiocyanate can be prepared by heating the thiocyanate of a heavy metal under pressure in an atmosphere of ammonia at 180°

$$Pb(CNS)_2+2NH_3=PbS+CH_5N_3,HCNS.$$

Levene and Senior (J. Biol. Chem. 1916, 25, 623) recommend the preparation of guanidine sulphate, starting with dicyanodiamide, and Schmidt (Arch. Pharm. 1916, 254, 626) prepares it from thio urea and from cyanamide (*see* D. R. P. 1909, 242,216 and 1912, 267,380); preparation from dicyanodiamide or its equivalents (Lidholm, Ber. 1913, 46, 156; Caro, Zeitsch. angew. Chem. 1910, 23, 2405).

According to Werner and Bell (Chem. Soc. Trans. 1920, 117, 1133), the best method of preparation consists in heating an intimate mixture of dicyanodiamide and dry ammonium thiocyanate to 120° for some hours, treating the melted mass with water, filtering, and concentrating the solution, and recrystallising the product; 90 p.c. yields are thus obtained. For further details the original memoir must be consulted.

Guanidine is a deliquescent crystalline solid, readily soluble in alcohol or water; it is volatile and strongly alkaline, absorbs carbon dioxide from the air and forms crystalline salts. The thermal value of the basic function of guanidine is +32·1 Cal., intermediate between that of barium hydroxide +31·7 Cal. and sodium hydroxide +36·4 Cal. (Matignon, Compt. rend. 1892, 113, 1432). Guanidine is decomposed into ammonia and urea on boiling with baryta water or dilute sulphuric acid (Ossikowsky, Bull. Soc. chim. 1872, [ii.] 18, 161; Baumann, Ber. 1873, 6, 1376); and is completely decomposed into carbon dioxide and ammonia by heating with concentrated acids or alkalis. Guanidine is decomposed, evolving two-thirds of its nitrogen, when mixed with sodium hypochlorite or hypobromite (Fenton, Chem. Soc. Trans. 1879, 14). The salts of guanidine, like the free base, part with their nitrogen quantitatively unless the hydrogen of the amino group has been substituted by $-COMe$, $-COPh$ or $-CONH_2$ (Cordier, Monatsh. 1912, 33, 759; *ibid.* 1914, 35, 9; *cf.* Kossel and Cameron, Zeitsch. physiol. Chem. 1911–12, 76, 457).

When guanidine hydrochloride is heated at 180°, ammonia is evolved and *biguanide* is formed, the reaction being similar to the formation of biuret from urea:

$$2HN:C(NH_2)$$
$$=NH_3+HN:C(NH_2)NH{\cdot}C(NH_2)NH$$

In its physiological action, guanidine is highly toxic; doses smaller than poisonous ones are in rabbits excreted unchanged in the urine (Pommerrenig, Beitr. Chem. Physiol. Path. 1902, i. 561; Garino, Arch. d. Farm. sperim, 22, 229, from Chem. Zentr. 1916, 11, 1047). The injection of guanidine hydrochloride into a rabbit is followed by symptoms which are almost identical with those of tetanus produced by extirpation of the parathyroid glands (Watanabe, J. Biol. Chem. 1918, 33, 253; 34, 51, 65, 73; 36, 531). Guanidine acts on frogs' muscles, producing spontaneous twitching and affecting their contractility, and it is supposed that the guanidine acts by combining with two different substances in the muscle, one of which is responsible for the twitching, and the other for the changes in contractility (Camis, J. physiol. 1909, 39, 73; Fühner, Arch. F. exp. Pathol. u. Pharm. 65, 401–27; Langley, J. of Physiol. 1916, 50, 419; Meighan, J. of Physiol. 1917, 51, 51). Although guanidine does not appear to be a normal oxidation product of arginine in the body (Pommerrenig, *l.c.*), it is found among the products of pancreatic auto-digestion (Kutscher and Otori, Zeitsch. physiol. Chem. 1904, 43, 93). Small quantities of guanidine, 0·1 per thousand, are injurious to chlorophyllous plants, whilst fungi utilise it as a source of nitrogen but not of carbon (Kawakita, Bull. Coll. Agr. Tōkyō, 1904, 6, 181; Kossawitz, Chem. Zentr. 1913, 1, 1279).

Many salts of guanidine give a yellowish-white flocculent precipitate with Nessler's reagent, which can thus be used as a test for small quantities of the salts of the base; a 0·05 p.c. aqueous solution of guanidine nitrate gives a bulky precipitate and a 0·01 p.c. solution is rendered turbid (Schulze, Ber. 1892, 25, 661). 22·8 parts of guanidine phosphotungstate are soluble in 100 parts of a mixture of acetone (4 vols.) with water (3 vols.) (Wechsler, Zeitsch. physiol. Chem. 1911, 73, 141; Drummond, Biochem. J. 1918, 12, 5). Another test for guanidine is the development of a deep yellow to orange-red coloration with alkali hypochlorites (de Coninck, Compt. rend. 1898, 126, 142). Certain guanidine derivatives precipitate colouring matter (Suida, Zeitsch. physiol. Chem. 1910, 68, 381). Guanidine is usually estimated as the picrate, the salt being collected on a Gooch asbestos filter, dried at 110° and weighed (Vozarik, Zeitsch. angew. Chem. 1902, 15, 670]; or it can be converted into the strongly alkaline carbonate and titrated with standard acid (Grossmann and Schück, Chem. Zeit. 1906, 30, 1205).

Guanidine forms crystalline salts with mineral and with organic acids; it also forms characteristic double salts. The *hydrochloride*

$$CH_5N_3,HCl$$

forms double salts with *mercuric chloride*

$$CH_5N_3,HCl,2HgCl_2$$

(Byk, J. pr. Chem. [ii.] 20, 233); with *gold chloride* $CH_5N_3,HCl,AuCl_3$, deep yellow, sparingly soluble needles (Hofmann, Ber. 1868, 1, 146); with *platinic chloride* $(CH_5N_3,HCl)_2,PtCl_4$, yellow needles, soluble in water, sparingly so in alcohol (Strecker, Annalen, 1861, 118, 160); with *platinic iodide* (Datta and Ghosh, J. Amer. Chem. Soc. 1914, 36, 1017). The *nitrate*, CH_5N_3,HNO_3, crystallises in large plates, m.p. 214°, 10·75 parts dissolve in 100 parts of water at 15·9°. The *compound* with silver nitrate $CH_5N_3,AgNO_3$ crystallises in needles, whilst the *compounds* with palladous trichloride and tribromide are brown or red crystals (Gutbier and Fellner, Zeitsch. anorg. Chem. 1916, 95, 169). The *nitrite* CH_5N_3,HNO_2 forms glittering prisms, m.p. 76°–78·5° (Lossen, Annalen, 1891, 265, 129). The *sulphate* $(CH_5N_3)_2,H_2SO_4$ crystallises in the regular system and is soluble in water (Bodewig,

J. 1876, 763); it forms a double salt with ***aluminium sulphate***

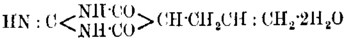
$$(CH_5N_3)_2,H_2SO_4,Al_2(SO_4)_3,12H_2O$$

crystallising in large, well-developed hexagonal prisms belonging to the scalenohedral class of the rhombohedral system, and having sp.gr. 1·806 at 13·5° (Ferraboschi, Proc. Camb. Phil. Soc. 1908, 14, 471). The *carbonate* $(CH_4N_3)_2,H_2CO_3$ forms octahedral or tetragonal prisms, sp. gr. 1·238–1·251 (Schröder, Ber. 1880, 13, 1072). The *metaphosphate* CH_5N_3,HPO_3 forms a fine crystalline precipitate (Pohl, Zeitsch. physiol. Chem. 1889, 13, 296). Guadinium molybdo-arsenate $(CN_3H_6)_3[As(Mo_2O_7)_3]$, yellow crystals, (Rosenheim, Weinberg, Pinsker, Zeitsch. anorg Chem. 1913, 84, 217). The *perchromate*

$$(CH_5N_3)_3CrO_8,H_2O$$

forms small brownish-yellow, double-refracting prisms, and yields the usual blue solution with ether and dilute sulphuric acid (Hofmann and Buchner, Ber. 1909, 42, 2773). The chlorate, white crystals, decomp. 148° (Datta, Choudhury, J. Amer. Chem. Soc. 1916, 38, 1079). The *thiocyanate* $CH_5N_3,HCNS$ has m.p. 118°, and 100 parts of water dissolve 73 parts at 0°, or 134·9 parts at 15° (Engel, Bull. Soc. chim. 1885, 44, 424). For preparation of the thiocyanate from ammonium thiocyanate *see* Krall (Chem. Soc. Trans. 1913, 103, 1378). The *platinothiocyanate* $(CH_5N_3)_2,H_2Pt(CNS)_6$ forms beautiful red crystals that blacken at 170°–175° (Guareschi, Chem. Zentr. 1891, ii. 620). The platinibromide $C_2H_{12}MoPlBrC_6$ lustrous red crystals of complicated structure (Gutbiera Ransch, J. pr. Chem. 1913, [ii], 88, 409–24). The *cyanurate* $(CH_5N_3)_3,(CNHO)_3$ forms silky needles (Bamberger, Ber. 1887, 20, 71). The *dioxalate* $CH_5N_3,C_2H_2O_4,H_2O$ is sparingly soluble (Strecker, *l.c.*). The *picrate* $CH_5N_3,C_6H_2(NO_2)_3OH$ is a sparingly soluble, yellow, crystalline salt, 1 part dissolves in 2630 parts of water at 9°, and it does not melt at 280° (Emich, Monatsh. 1891, 12, 24). According to von Cordier (Chem. Zentr. 1906, i. 340), guanidine picrate exhibits stereoisomerism. The salt, as usually prepared, forms dark yellow plates that, owing to repeated twinning, have a hook-like structure, but when guanidine prepared by decomposing methylguanidine sulphate with barium hydroxide is used, the picrate crystallises in rosettes of bright yellow needles. The two forms are identical in composition, sp.gr., temperature of decomposition, and electric conductivity, but differ in colour, crystalline form and solubility, 100 parts of water dissolve 0·037 part of the plates at 0°, 0·061 at 20°, and 0·574 at 80° The solubility of the needles is 0·043, 0·060, 0·800 at these temperatures respectively. One form cannot be converted into the other by crystallisation, and the author suggests that they are stereoisomerides, the plates being the stable modification, $NH_2\cdot\underset{NH}{C}\cdot NH_2\cdot C_6H_3O_7N_3$, and the needles the labile $NH_2\cdot\underset{HN}{C}\cdot NH_2\cdot C_6H_3O_7N_3$. The *benzenesulphonate* has m.p. 200°, the *p-toluene-sulphonate*, m.p. 206°, and the *α- and β-naphthalenesulphonates*, m.p. 257° (Remsen and Garner, Amer. Chem. J. 1901, 25, 173). The 4-*nitroacetylanthranilate* has m.p. 247° (corr.) (Bogert and Klaber, J. Amer. Chem. Soc. 1908, 30, 807). The *acetate* $CH_5N_3\cdot C_2H_4O_2$ forms shining needles, m.p. 229°–230° (Ostrogovich, Gazz. chim. ital. 1897, 27, i. 223). The *picrolonate* $CH_5N_3\cdot C_{10}H_8O_5N_4$ is soluble in alcohol (Schenck, Zeitsch. physiol. Chem. 1905, 44, 427). A number of salts of guanidine (*guanidinium* salts) with iso- and hetero-poly acids have been prepared (Gutbier, Mehler and Ottenstein, Zeitsch. anorg. Chem. 1914, 89, 313, 333, 343; Rosenheim and Garfunkel, Ber. 1911, 44, 1865; Rosenheim and Felix, Zeitsch. anorg. Chem. 1913, 79, 292; Rosenheim and Schwer *ibid.* 1914, 89, 224; Rosenheim and Traube, *ibid.* 1915, 91, 75; Rosenheim, Zeitsch. elektro. Chem. 1911, 17, 694)

Allyl Malonyl Guanidine

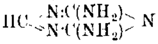


$$HN : C{<}\genfrac{}{}{0pt}{}{NH\cdot CO}{NH\cdot CO}{>}CH\cdot CH_2CH : CH_2\cdot 2H_2O$$

m.p. 265°–266°, crystallises from acetic acid in hexagonal plates (Johnson and Hill, Amer. Chem. J. 1911, 46, 537).

For guanido-glycylglycine and the introduction of guanidine into the polypeptide molecule (*see* Clementi, Gazz. chim. ital. 1915, 45, 56–59, and 276–280).

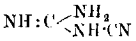
Guanamines. When the guanidine salts of the first seven of the fatty acid series are heated at 220°–230°, water and ammonia are eliminated and heterocyclic bases called *guanamines* are formed: these are well-characterised crystalline compounds. *Formoguanamine*



$$HC{<}\genfrac{}{}{0pt}{}{N{:}C(NH_2)}{N\cdot C(NH_2)}{>}N$$

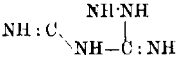
melts and decomposes at a high temperature; *acetyguanamine* $CH_3\cdot C{<}\genfrac{}{}{0pt}{}{N{:}C(NH_2)}{N\cdot C(NH_2)}{>}N$ melts at 265°; *propionoguanamine* blackens at 300°; *œnanthoguanamine* melts at 130° (Nencki, Ber. 1874, 7, 1584; Haaf, J. pr Chem. 1891, [ii.] 43, 75).

Cyanoguanidine (*dicyandiamide*)



$$NH : C{<}\genfrac{}{}{0pt}{}{NH_2}{NH\cdot CN}$$

results from the polymerization of cyanamide; it can be prepared from calcium or sodium cyanamide (Chem. Zentr. 1905, 11, 1530), m.p. 205°. It is a neutral body. Ammonia converts it into diguanide; dilute acids into guanyl urea. Heated with hydrazine hydrochloride in alcoholic solution it gives guanazole



$$NH : C\genfrac{}{}{0pt}{}{\diagup NH\cdot NH}{\diagdown NH-C : NH}$$

m.p. 206° (Ber. 27 R.583). A mixture of cyanoguanidine and acetamidine hydrochloride gradually heated to 230° yields 4 : 6-diamine-2-methyl-1 : 3 : 5 triazine dihydrochloride, and, similarly, cyanoguanidine and benzamidine yield the corresponding phenyl derivative, m.p. 225°; or the same triazine derivatives may be obtained on heating cyanoguanidine with aceto nitrite in a sealed tube for three hours at 225°–230°, or with benzo nitrite for four or five hours at 190°–200° (Ostrogovich, Atti. R. Accad. Lincei, 1911, [v.], 20, 1, 182, and 249.

When cyanoguanidine is heated with an ethereal solution of thioacetic acid until the evolution of hydrogen sulphide ceases, 6-thiol-2-inimo-4-methyl-1 : 3 : 5-triazine is formed; small colourless needles which decompose without melting (Ostrogovich, *ibid.* 1912, [v.], 21, 1, 213.

Chloroguanidine CH_4ClN_3, obtained by the action of bleaching powder solution on guanidine carbonate in ice water, forms a pale yellow crystalline powder that decomposes at 150° (Kamenski, Ber. 1878, 11, 1602).

Bromoguanidine CH_4BrN_3, formed from equimolecular proportions of bromine and guanidine carbonate, crystallises in yellow needles. By the action of 3 mols. bromine on 1 mol. guanidine carbonate, the *compound*

$$CH_5N_3\cdot HBr\cdot Br_2$$

is formed, crystallising in dark red prisms. The corresponding *iodine compound* $CH_5N_3\cdot HI\cdot I_2$ crystallises in prisms the colour of iodine (Kamenski, *l.c.*).

Nitroguanidine $NH:C(NH_2)NH\cdot NO_2$ was first prepared by Jousselin (Compt. rend. 1877, 85, 548; 1879, 88, 814, 1086) by the action of fuming nitric acid and nitric oxide on guanidine nitrate, and called by him nitrosoguanidine. Pellizzari (Gazz. chim. ital. 1891, 21, ii. 405) showed that it was the *nitro* compound, and his results were confirmed by Thiele (Annalen, 1892, 270, 1), who also prepared it by the action of fuming nitric acid and sulphuric acid on guanidine thiocyanate. It crystallises from water in colourless needles, melts and decomposes at 230° with evolution of ammonia; it dissolves in 372–375 parts of water at 19·3°, or in 11 parts of boiling water. The heat of combustion at constant pressure is +210·3 Cal. and the heat of formation from its elements is +22 Cal. (Matignon, Compt. rend. 1892, 114, 1432). The *silver* derivative $CH_3N_4O_2Ag$ is colourless and almost insoluble in water; the *nitrate* $CH_4O_2N_4\cdot HNO_3$ is crystalline and melts at 147°; the *hydrochloride* $CH_4O_2N_4\cdot HCl$ crystallises in plates or prisms.

Nitrosoguanidine $NH:C(NH_2)NH\cdot NO$ is obtained by the partial reduction of nitroguanidine with zinc dust and sulphuric acid. It forms yellow needles, explodes violently at 160°–165°, is soluble in alkalis and reprecipitated by carbon dioxide; it also gives the Liebermann reaction. The alkali solutions give a beautiful purple coloration with ferrous salts. The *silver salt* CH_3ON_4Ag is a colourless explosive precipitate; the *copper salt* $(CH_3ON_4)_2Cu$ is reddish-brown, and the *nickel salt* $(CH_3ON_4)_2Ni$ is vermilion-red (Thiele, Annalen, 1893, 273, 133). According to Hantzsch, Schümann, Engler (Ber. 1899, 32, 575, 1703), nitrosoguanidine is a true nitrosamine and its constitution is represented by the formula $NH:C(NH_2)NH\cdot NO$, since it has a neutral reaction, yields mainly nitrous acid and not nitrogen when decomposed by acids, and does not interact with phosphorus pentachloride or acetyl chloride. On the other hand, Whiteley (Chem. Soc. Trans. 1903, 31) and Tschugaeff (Ber. 1906, 39, 3383) consider that the coloured metallic derivatives are salts of the tautomeric diazo-hydrate form $HN:C(NH_2)N:N\cdot OH$.

Aminoguanidine $HN:C(NH_2)NH\cdot NH_2$, is obtained by reducing nitroguanidine with zinc dust and acetic acid at 40° until a test portion develops no coloration with ferrous sulphate and an alkali (Thiele, Annalen, 1892, 270, 23. The mixture is filtered, the filtrate evaporated till it is only feebly acid, and the aminoguanidine bicarbonate precipitated in the cold by adding a concentrated solution of alkali bicarbonate (D. R. P. 59241). Also prepared by heating an alcoholic solution of hydrazinehydrochloride, and cyanamide in a reflux apparatus (Pellizzari and Cuneo, Gazz. chim. ital. 1894, 24, i. 450; Pellizzari and Gaiter (Gazz. chim. ital. 1914, 44, ii, 72). A yield of 81 p.c. of the theoretical is obtained by the electrolytic reduction of the nitro compound, suspended in water slightly acidified with sulphuric acid, using a tin cathode and a current density of 250 amperes per square metre and a temperature of 10° (Boehringer and Söhne, D. R. P. 167637); *cf.* also Ponzio and Gastaldi (Gazz. chim. ital. 1914, 44, 1, 257).

Aminoguanidine is crystalline, soluble in water or alcohol, decomposes on boiling with dilute acids or alkalis, yielding first semicarbazide and finally ammonia, carbon dioxide, and hydrazine (Curtius, Ber. 1896, 29, 759). For the toxicity of guanidine and its amino derivatives, *v.* Garino (Arch. Farm. sper. 1916, 22, 229). Aminoguanidine forms crystalline salts with mineral acids: the *hydrochloride* CH_6N_4,HCl forms large prisms, m.p. 163°; the hydrobromide, prismatic needles, m.p. 149° (decomp.); the *double salt* with platinic chloride

$$(CH_6N_4,HCl)_2,PtCl_4$$

is a yellow precipitate, m.p. 145°–146°; the *nitrate* CH_6N_4,HNO_3 forms large shining plates, m.p. 144°; 100 parts of water dissolve 12·01 parts at 15·9°; the *sulphate* $(CH_6N_4)_2,H_2SO_4,H_2O$ crystallises in needles, m.p. 207°–208°; the *bisulphate* CH_6N_4,H_2SO_4 crystallises in large plates, m.p. 161°; the *picrate* $CH_6N_4,C_6H_3O_7N_3$ is precipitated as yellow needles from hot water. The *copper compounds* $Cu(CH_5N_4)_2,2HNO_3$ and $Cu(CH_5N_4)_2, H_2SO_4$ are violet crystalline precipitates; the *bicarbonate* CH_6N_4,H_2CO_3 (Thiele, Annalen, 1898, 302, 332) melts at 172° and is almost insoluble in cold water.

Acetaminoguanidine $CH_5N_4(C_2H_3O)$ forms a crystalline *nitrate*, m.p. 85°–90° and *picrate*; *formylaminoguanidine nitrate*

$$HNO_3,H_2N\cdot C(NH)NH\cdot NH\cdot CHO$$

melts at 143°, the *picrate* melts at 193°; *oxalylaminoguanidine* $HN:C(NH_2)NH\cdot NH\cdot CO\cdot CO_2H$ melts at 231°–232° (Thiele and Manchot, Annalen, 1898, 303, 37).

Aminoguanidine and its alkyl and aryl derivatives contain the grouping $-NH\cdot NH_2$, present in hydrazines, and semicarbazide, and like them readily form condensation products with aldehydes, ketones, sugars, and ketonic acids; these are usually well characterised crystalline compounds, forming crystalline salts with mineral and organic acids. For the condensation products with aldehyde, chloraldehyde, chloral, *v.* Thiele and Dralle (Annalen, 1898, 302, 278); with benzaldehyde, *v.* Thiele (*ibid.* 1892, 270, 1), Wedekind (Ber. 1897, 30, 444); with diacetyl, acetylacetone, acetonylacetone, *v.* Thiele and Dralle (*l.c.*); with galactose, glucose, and lactose, *v.* Wolff (Ber. 1895, 28, 2613); with glyoxylic acid, *v.* Thiele and Dralle (*l.c.*), Doebner and Gärtner (Annalen, 1901, 315, 1); with pyruvic acid, *v.* Wedekind and Bronstein (*ibid.* 1899, 307, 297). For the preparation and properties of *alkyl* and *aryl* substituted derivatives of aminoguanidine, *v.* Pellizzari and Cuneo (Gazz. chim. ital. 1894, 24, i. 450), Pellizzari and Rickards (*ibid.* 1901, 31,

. 526). Sodium nitrite and a solution of minoguanidine dinitrate yield a β-nitroso ydrazine derivative

$NH_2{\cdot}C{\cdot}(NH){\cdot}NH{\cdot}NH{\cdot}N{=}N{\cdot}C(:NH){\cdot}NH{\cdot}NH{\cdot}NO$

which is extremely stable. The sulphate $C_2H_7N_{10})_2SO_4$, crystallises in long colourless prisms. Hofmann, Hock, Kirmreuther (Annalen, 1911, 380, 131).

Diaminoguanidine $HN.C(NH{\cdot}NH_2)_2$ does not exist in the free state; its *hydrobromide* CH_7N_5,HBr is formed by the action of cyanogen bromide (1 mol.) on hydrazine (2 mols.); it crystallises in plates, m.p. 167°; the *picrate*, $CH_7N_5,C_6H_3O_7N_3$, melts at 191°; the *hydrochloride* at 185°; the *nitrate* at 143°; the *platinochloride* at 172°–173°; all the salts reduce Fehling solution and ammoniacal silver nitrate solution. *Dibenzylidenediaminoguanidine*

$HN:C(NH{\cdot}N:CHPh)_2$

yellow crystals, m.p. 180°; *disalicylidenediaminoguanidine* $AH:C(AH{\cdot}N:CH{\cdot}C_6H_4OH)_2$ yellow prisms, m.p. 201°–203°; the *hydrobromide* melts at 240°. *Dibenzoyldiaminoguanidine*

$NH:C(NH{\cdot}NHC_6H_5CO)_2$

m.p. 210°–211°; the *hydrobromide* melts at 243°, and the *hydrochloride* at 230°, the *nitrate* at 211° 212° (Pellizzari and Cantoni, Gazz. chim. ital. 1905, 35, i. 291); Pellizzari and Gaiter (*l.c.*); Gaiter (*ibid.* 1915, 45, 450).

Triaminoguanidine $NH_2{\cdot}N:C(NH{\cdot}NH_2)_2$ does not exist in the free state; its salts may be obtained by heating concentrated solutions of the salts of either guanidine or its amino, or its diamino derivative with hydrazine hydrate. The salts readily react with aldehydes. The *nitrate* colourless needles has m.p. 210° (decomp.); the *hydrochloride*, m.p. 231°; *tribenzylidenetriaminoguanidine*, small yellow needles, m.p. 198°; *triaminoguanidinethiocyanate*, m.p. 136°; the *picrate* $CH_8N_6,C_6H_3O_7N_3$, m.p. 171°, Pellizzari and Gaiter (*l.c.*).

Dihydroxyguanidine hydrobromide

$HN:C(NH{\cdot}OH)_2,HBr$

is formed by the interaction of cyanogen bromide and hydroxylamine in methyl alcohol and ether at −20°: it forms colourless, flat, hygroscopic needles that decompose at 95° (Wieland, Ber. 1905, 38, 1445).

Methylguanidine $HN:C(NH_2)NHMe$ has been isolated from extract of muscle (Gulewitsch, Zeitsch. physiol. Chem. 1906, 47, 471; *see also* Ewins (Bio-Chem. J. 1916, 103); for its presence in urine of dogs *see* Koch (J. of Biol. Chem. 1913, 15, 313)), and is prepared by boiling creatine with mercuric or lead oxide and dilute sulphuric acid (Dessaignes, Annalen, 1854, 92, 407; 1856, 97, 340). It can be synthesised from methylamine hydrochloride and cyanamide (Erlenmeyer, Ber. 1870, 3, 896). It is a strongly alkaline, volatile, crystalline substance, and liberates ammonia and methylamine on heating with potassium hydroxide. The *aurichloride* $C_2H_7N_3,HCl,AuCl_3$ melts at 198°–200°; the *platinichloride* $(C_2H_7N_3,HCl)_2,PtCl_4$ melts at 194°–195° (Schenck, Arch. Pharm. 1909, 247, 466). The *oxalate* $(C_2H_7N_4)_2,C_2H_2O_4,2H_2O$ is crystalline and soluble in water. The *picrate* crystallises from water in two distinct modifications (Gulewitsch, *l.c.*). The *picrolonate*

$C_2H_7N_3,C_{10}H_8O_5N_4$

melts at 291° (Wheeler and Jamieson, J. Biol. Chem. 1908, 4, 111). Eleven methylated guanidines are possible: three of these, containing the grouping $NMe:C(NH_2)N{=}$ have not been obtained; *S-αβγ-Trimethylguanidine*, is formed whenever the conditions are in any way favourable (Schenck, Arch. Pharm. 1911, 249, 463; *ibid.* 1912, 250, 306; Zeitsch. physiol. Chem. 1912, 77, 328).

For other *alkyl* and *aryl* substituted derivatives of guanidine, some of which have therapeutic properties, *v.* Strakosch (Ber. 1872, 5, 692); Tatarinow (J. 1879, 401); Noah (Ber. 1890, 23, 2196); Hofmann (*ibid.* 1869, 2, 601); Fischer (*ibid.* 1897, 30, 2414); Alway and Vail (Amer. Chem. J. 1902, 28, 158); Kämpf (Ber. 1904, 37, 1681); Reidel (D. R. PP. 1892, 66550, 1898, 104361); Schmidt (Arch. Pharm. 1911, 249, 465, and 473; *ibid.* 1912, 250, 311). For *acyl* derivatives *see* Traube (Ber. 1910, 43, 3586); Pierron (Compt. rend. 1910, 151, 1364); Wheeler and Johnson (Amer. Chem. J. 1901, 26, 417). Formyl guanidine

$NH_2C(NH){\cdot}NH{\cdot}CHO$

has m.p. 178° (decomp.); acetyl guanidine, m.p. 185°; acetyl guanidine hydrochloride, m.p. 145° (Korndörfer, Arch. Pharm. 1903, 241, 449, gives m.p. 142°); benzoyl phenylguanidine $C_6H_5CONHC(:NH)NHPh$, m.p. 91°–92°. *m*-Tolylbenzoylguanidine

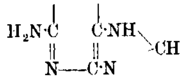
$CH_3{\cdot}C_6H_4{\cdot}NH{\cdot}C(:NH){\cdot}NH{\cdot}COC_6H_5$

begins to soften 71°, the hydrochloride melts at 170°.

Guanidine forms condensation products with *dicarboxylic acids* (Traube, Ber. 1893, 26, 2551; Ruheman and Stapleton, Chem. Soc. Trans. 1900, 805; Kaess and Gruszkiewicz, Ber. 1902, 35, 3600); with *β-ketonic acids* (Jaeger, Annalen, 1891, 262, 365); with *β-diketones* (Evans, J. pr. Chem. 1892, 45, 489; Wense, Ber. 1886, 19, 761); with *malononitrile* (Merck, D. R. PP. 165692, 165693); with *ethyl cyanacetate* (Traube, D. R. P. 1900, 115253).

Guanidine forms *compounds* with sugars containing 3 mols. of sugar and 1 mol. of guanidine; these exhibit mutarotation and have a lower optical activity than the sugars from which they are derived (Morrell and Bellars, Chem. Soc. Trans. 1907, 1010). M. A. W.

GUANINE, *2-amino-6-oxypirine*,



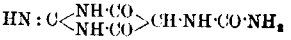
was discovered by Unger in guano in 1844 (Annalen, 51, 395; 58, 18; 59, 58), and though Hoppe-Seyler failed to find it in the excrement of fowls and geese, Haeter obtained it from the excrement of a heron (*Ardea cinerea*) fed on fish and flesh (Med. Chem. Untersuch. 1871, 582); Will and Gorup Besanez found it in the excrement of a spider, in the organ of Bojanus of the mussel, and in the green gland of the crayfish (*cp.* Weinland, Zeit. Biol. 25, 390); and Pecile found 0·0068 gram of guanine per litre in the urine of a pig fed on bran, and in an unhealthy condition (Annalen, 1876, 183, 141). In addition to its occurrence among the excretory products of the animal, guanine is fairly widely distributed throughout the tissues; thus it is found in the liver, Smorodinzeff (Zeitsch. physiol. Chem. 1912, 80, 231; in muscle (Bennett, J. Biol. Chem. 1912, 11, 221); and it occurs, together with hypoxanthine, in the protamine from salmon roe, forming 6–8 p.c. of the ripe organ (Piccard, Ber. 1874, 7, 1714); it occurs in the pancreas, spleen, liver, and muscle of the ox, in quantities varying from 0·020 to 0·746 p.c. (Braginsky, Zeitsch. physiol. Chem. 1883, 8, 395; Kossel, *ibid.* 404; Schindler, *ibid.* 1889, 13, 432); and it is found in the skin of fishes (Ewald and Kruckenberg, Chem. Zentr. 1883, 705; *see* Heller, Intern. Zeitsch. Biol. 3, 106 for possible connection between bioluminescence and guanine). Guanine is widely spread throughout the vegetable kingdom, Schützenberger found it, together with other purine bases, in yeast extract (Compt. rend. 1874, 78; Chem. Zentr. 1877, 73); Drummond and Funk in rice polishings (Bio-Chem. J. 1914, 8, 598). Schulze and Bosshard isolated it, together with hypoxanthine and xanthine, from young potato tubers, sugar beet, leaf buds of plane and maple, bark of plane, from lupins, red clover, vetch, young grass, and oats (Zeitsch, physio'. Chem. 1884, 9, 420); and v. Lippmann obtained it from beet juice (Ber. 1896, 29, 2645); molasses residues boiled with copper sulphate and sodium hydroxide yield about 0·04 p.c. guanine pentoside

$$C_5H_8O_4,C_5H_5N_5O\cdot 2H_2O$$

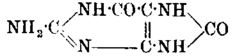
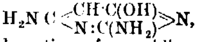
(Andrlik, Zeitsch. Zuckerind. Böhm. 1911, 35, 437). This is identical with the guanosine obtained from nucleic acid (Levene and Jacobs, Ber. 1909, 42, 2474; Biochem. Zeitsch. 1910, 28, 127); and with *vernine* (guanine-*d*-ribose), $[\alpha]_D^{20°} - 8\cdot 4°$ (Schulze and Trier, Zeitsch. physiol Chem. 1911–1912, 76, 145; Smolenski, Chem. Zentr. 1912, 2, 769). According to Levene and Mandel (Biochem. Zeitsch. 1908, 10, 215; *see also* Jones and Richards, J. Biol. Chem. 1915, 20, 25), guanine is one of the cleavage products of nucleic acid, when the hydrolysis is effected by acetic acid in the presence of lead acetate at 150°; *cf.* Levene and Jacobs (J. Biol. Chem. 1912, 377); Scaffidi (Biochem. Zeitsch. 47, 215); it is found among the products of steam-heated soils, Lathrop (J. Amer. Chem. Soc. 1912, 34, 1260).

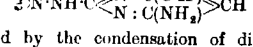
Guanine exists in guano partly as the calcium compound, partly in substances like nuclein; from these it is liberated by boiling for 4 hours with dilute sulphuric acid, the liquid is cooled and filtered, and the filtrate made alkaline with sodium hydroxide and again filtered. The guanine and uric acid are precipitated in the filtrate by the addition of ammoniacal silver solution, the precipitate washed with cold and hot water, and then decomposed by hot dilute hydrochloric acid, the silver chloride filtered off, the filtrate decolorised with animal charcoal, and the guanine precipitated by ammonia, a small quantity of urea in hot nitric acid is added, and the mixture set aside to crystallise. The guanine nitrate now free from uric acid is dissolved in dilute sodium hydroxide and the guanine precipitated by the addition of ammonium chloride, this last operation removing the xanthine (Wulff, Zeitsch. physiol. Chem. 1893, 17, 468). It may be precipitated as the phosphotungstate—for the solubility of this in a mixture of acetone and water, *see* Wechsler (Zeitsch. physiol. Chem. 1911, 73, 141).

Fischer (Ber. 1897, 30, 559) has shown that guanine is 2-amino-6-oxypurine from the fact that *imino-ψ-uric acid*



$$HN:C<\begin{matrix}NH\cdot CO\\ NH\cdot CO\end{matrix}>CH\cdot NH\cdot CO\cdot NH_2$$

obtained synthetically by Traube (Ber. 1893, 26, 2551) from guanidine and ethylmalonate, yields, on treatment with hydrochloric acid (sp.gr. 1·19), at 120°, the same 2-*amino*-6 : 8-*dioxypurine*  $NH_2\cdot C\begin{matrix}\diagup NH\cdot CO\cdot C\cdot NH\diagdown\\ \quad\quad\quad\quad\| \\ \diagdown\!\!\diagdown N\text{———}C\cdot NH\diagup\end{matrix}CO$ as is obtained from *bromoguanine* $C_5H_4BrON_5$ (Fischer and Reese, Annalen, 1883, 221, 342) by the action of hydrochloric acid at 130°. Further, a synthetic guanine, identical in every way with the natural product, is obtained when 6-*oxy*-2 : 8-*dichloropurine* is heated with alcoholic ammonia, and the resulting *chloroguanine* reduced by means of hydriodic acid (Fischer, Ber. 1897, 30, 2226). The synthetical production of guanine has also been effected by Traube (Ber. 1900, 33, 1371) from 2 : 4-*diamino*-6-*hydroxy-pyrimidine*  $H_2N\,C<\begin{matrix}CH\cdot C(OH)\\ N:C(NH_2)\end{matrix}>N$, obtained by the condensation of guanidine and ethyl cyanoacetate in the presence of sodium ethoxide. The nitroso derivative of this compound yields, on reduction with ammonium sulphide, 2 : 4 : 5-*triamino*-6-*hydroxypyrimidine*, which, when heated with an equivalent amount of sodium formate and 8–10 times its weight of anhydrous formic acid, is converted into guanine. A similar synthetic production of guanine from 2-*cyanamino*-4-*amino*-6-*hydroxypyrimidine*



$$CN\cdot NH\cdot C<\begin{matrix}N\cdot C(OH)\\ N:C(NH_2)\end{matrix}>CH$$

obtained by the condensation of dicyanodiamide and ethyl cyanoacetate in the presence of sodium ethoxide, forms the subject of certain patents of Merck (D. R. PP. 1905, 158591, 162336).

Guanine is an amorphous powder, insoluble in water, alcohol, or ether, but soluble in acids or alkalis, forming salts of a di-acid base, or dibasic acid respectively. It can be obtained in the form of small rhombic crystals when the freshly precipitated compound is dissolved in a large excess of ammonia at 30°–35°, and the filtered solution allowed to evaporate slowly (Drechsel, J. pr. Chem. 1881, 24, 44); or in crystals resembling those of creatinine zinc chloride, when a warm dilute alkaline solution (1 : 2000) is mixed with about one-third its volume of alcohol, acidified with acetic acid and allowed to cool (Horbaczewski, Zeitsch. physiol. Chem. 1897, 23, 226).

The administration of guanine as food to rabbits produces neither increase in purine excretion nor pathological changes in the kidney; but subcutaneous or intravenous injections of guanine dissolved in caustic soda, cause a great increase of purine substances, especially uric acid, in the urine (Schittenhelm, Chem. Zentr. 1902, i. 1306; Schittenhelm and Bendix, Zeitsch. physiol. Chem. 1905, 43, 365; Ewald, Zeitsch. exp. Path. u. Ther. 2, 348), and diminishes the arterial blood pressure (Desgrez *guaranatannic acid*, appears to resemble the chlorogenic acid obtained from coffee (Gorter, Annalen, 358, 327; 359, 217) rather than catechin, but is not identical with either of these substances (Annals Trop. Med. 4, 115). G. B.

GUATANNIN. Syn. for guaicol tanno-cinnamate.

GUAVA. The fruit of *Psidium Guajava* (Linn.). Prinsen-Geerligs (Chem. Zeit. 1897, 21, 719), gives the following data:

Average wt. in grammes	The fruit consists of			The flesh contains		
	Flesh	Skin	Seeds	Glu-cose p.c.	Levu-lose p.c.	Su-crose p.c.
65·0	85·0	12·0	3·0	2·0	0·5	1·7

H. I.

GUERNSEY BLUE. A colouring matter belonging to the INDULINE group (*q.v.*).

GUIASANOL. Trade name for diethylglycocoll guaiacol hydrochloride.

GUIGNET'S GREEN *v.* CHROMIUM.

GUINEA GREEN B. The sodium salt of the disulphonic acid of diethyl-dibenzyl-di-amino-triphenyl-carbinol. Is a dark green powder resembling Light-green S or Acid Green, *v.* TRIPHENYLMETHANE COLOURING MATTERS.

GULAMAN DAGAT. A seaweed of the genus *Gracilaria*, found throughout the Philippine Islands; may be used as a substitute for gelatin where only the physical properties of gelatin are important. It is not a protein, and contains less than 1 p.c. of nitrogen and is of little value as a food. It resembles agar-agar, but has less strongly marked solidifying power, does not melt so freely, is not so fluid when melted, and solidifies at a higher temperature; it is unsuitable for bacteriological work owing to its low crushing pressure and slight surface strength (Wells, Philippine J. Sci. 1916, 11, 267; Analyst, 1917, 42, 391).

GULAUCHA, GULOE, and **GILOE.** Indian names for *Tinospora cordifolia* (Miers.). This plant flourishes in India, the drug being sold extensively in the bazaars as a tonic and antiperiodic, in the form of cylindrical pieces 2–5 cm. long and 1–5 cm. in diameter. It is a perennial creeper, climbing to the summits of the highest trees, its branches putting forth roots which, reaching to the ground, initiate a fresh growth. Roots, stems, and leaves are equally in demand as a drug. The Indian pharmacopœia commends its use as a tincture, 4–8 c.c. *in die*); as an extract (0·6–1 gram *per diem*) in the form of pills; and as an infusion (1 : 10), of which 60–90 c.c. are to be taken thrice a day. The stems contain *verberin*, an uncrystallisable bitter substance, changed by dilute sulphuric acid into a glucoside, and a bitter kind of starch meal known as 'palo' (J. Soc. Chem. Ind. 6, 49).

GUM RESINS. This article includes the more important members of that group of products which consist essentially of a mixture of gum and resin. They are generally the exudated milky juice of plants dried by spontaneous evaporation. When triturated with water they give more or less perfect emulsions, the gum dissolving and the resin remaining insoluble. Conversely, alcohol dissolves the resin but not the gum. 10–15 parts of a 60 p.c. aqueous chloral hydrate solution dissolve both, leaving impurities such as sand and woody fibre behind. From the solution alcohol precipitates the gum, leaving the resin in solution. Compare introduction to article RESINS.

Ammoniacum, B.P.; *Gummi-resina ammoniacum. Gomme-résine ammoniaque*, Fr.; *Ammoniak Gummiharz*, Ger.

Persian ammoniacum. The ammoniacum of the early Greek physicians came from Africa, and was probably that variety known as African ammoniacum. The drug, which has however since the tenth century been an article of European commerce, is obtained from Persia and neighbouring districts, reaching our markets according to Dymock (Pharm. J. [iii.] 6, 321) now generally by way of Bombay. It is the inspissated juice collected from the stems of the *Dorema Ammoniacum* (D. Don). For plates *v.* Bentl. a. Trim. 131. This plant attains a height of 6–8 feet, and the flow of juice from its stem is caused by punctures made by beetles.

The gum-resin occurs in commerce as brittle grains or tears, or roundish lumps, pale yellow externally and waxy milky-white within. It softens readily when warmed. In taste it is bitter and acrid, and it possesses a characteristic odour. Triturated with water it forms an emulsion. A very complete account of the literature of ammoniacum, including the result of the examination of some twenty specimens, will be found in the memoir of Hirschsohn (Pharm. Zeit. 1875, 225; Pharm. J. [iii.] 7, 612, 710, and 770). The sp.gr. of ammoniacum is 1·19–1·21, and 3 parts of it dissolve in 4 of alcohol. Hypochlorites, as for example a solution of bleaching powder, impart to it a bright orange colour, a character that serves to distinguish it from the African variety which is not affected by these reagents. The allied gum-resin galbanum also gives no colour reaction with hypochlorites.

Ammoniacum consists essentially of *resin*, *gum*, and a small proportion of *volatile oil*. The *resin* constitutes 70 p.c. of good specimens of the drug. A sample of ammoniacum examined by Luz (Arch. Pharm. 233, 540) contained 4·5 p.c. of water, 69 p.c. of resin, 22·7 p.c. of substances soluble in water, and 3·5 p.c. of substances, other than resin, insoluble in water. A considerable amount of salicylic acid was present, but no aldehydes or terpenes. Normal butyric and valeric acids were also present largely in combination with a resin alcohol *ammoresinotannol* $C_{18}H_{30}O_3$, a chocolate-brown, tasteless and odourless powder, soluble in alkalis and acids. The resin consists essentially of ammoresinotannol salicylate. It melts at from 35° to 50°, is soluble in alcohol, chloroform, glacial acetic acid, sulphuric acid, and alkalis, partly soluble in carbon disulphide, benzene, and solution of ammonia, and insoluble in light petroleum. Sommer (J. 1859, 573) was unable to obtain umbelliferone from the gum-resin, but resorcinol, $C_6H_4(OH)_2$, and protocatechuic acid, $C_6H_3(OH)_2COOH$, are formed when it is fused with potash (Hlasiwetz and Barth, Annalen, 130, 354). It yields styphnic acid, trinitroresorcinol, $C_6H(NO_2)_3(OH)_2$, when treated with nitric acid (Will and Böttger, Annalen, 58, 269; *cf.* Schwanert, *ibid.* 128, 123).

Ammoniacum gum is partly soluble and partly insoluble in water. The insoluble portion, which constitutes a fourth of the gummy constituents, appears to be identical with the similar bassorin-like gums which occur in asafœtida and galbanum. When treated with 20 p.c. hydrochloric acid, besides humus substances, it yields lævulic acid, and, on oxidising with nitric acid, 31·3 p.c. of mucic acid (equivalent to 41·75 p.c. of galactose), but no saccharic acid. When distilled with dilute hydrochloric acid, it yields 9·35 p.c. furfuraldehyde (equivalent to 16·67 p.c. of arabinose), and when boiled with dilute sulphuric acid reducing sugars are obtained, consisting chiefly of galactose (Frischmuth, Chem. Zentr. 1897, ii. 1078).

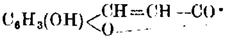
Hirschsohn obtained no volatile oil by distillation with water, but light petroleum gave him 1·4–6·7 p.c. of volatile oily residues. Flückiger and Hanbury describe the oil as unlike that of galbanum, possessing in a high degree the odour of the drug, and being free from sulphur.

To test ammoniacum for galbanum resin 5 grams is boiled with 15 grams of strong hydrochloric acid for 15 minutes, 15 c.c. of water is then added, and the liquid filtered through a wetted, double filter; ammonia is added to the clear filtrate, when a blue fluorescence reveals the presence of galbanum (Dieterich. Chem. Zentr. 1896, ii. 1137). For method of examination and table giving analytical constants, *see* Dieterich, *l.c.*, and Pharm. Centh. 40, 467.

Ammoniacum is employed in medicine internally as an expectorant, and externally as a constituent of plasters.

African ammoniacum. This, according to Hanbury (Pharm. J. [iii.] 3, 741), is the ammoniacum of Dioscorides and the older writers. It is derived, according to Lindley (Pereira, Mat. Med. 1853, 1715), from the *Ferula tingitana* (Linn.), a plant inhabiting the African coast of the Mediterranean Sea.

African ammoniacum, which is scarcely known in European markets, is described by Pereira as consisting of dark-coloured masses which internally have much the appearance of the Persian variety. The odour is, however, quite distinct. It forms an emulsion with water. Moss examined a specimen in 1873 (Pharm. J. [iii.] 3, 742) which consisted of *resin* 67·76 p.c., *gum* 9·01 p.c., *water* and *volatile oil* 4·29 p.c., and *bassorin* and *insoluble matter* 18·85 p.c. It contained 13·47 p.c. of *ash.* It softened between the fingers more readily than Persian ammoniacum. Similar results were obtained by Hirschsohn. By distilling it, however, the last observer isolated *umbelliferone*



$$C_6H_3(OH)<\begin{matrix}CH{=}CH-CO\\O\text{------}\end{matrix}$$

Goldschmiedt (Ber. 11, 850) announces that by fusion with potash African ammoniacum yields resorcinol, together with *an acid* $C_{10}H_{10}O_6$. This acid is not produced when the Persian drug is similarly treated.

Asafœtida; *Asafetida,* B.P.; *Asafœtida,* U.S.P.; *Gummi-resina Asafœtida. Asafœtida* Fr.; *Asant, Stinkasant, Teufelsdreck,* Ger.

Gum-resin asafœtida is the dried juice of the roots of two large herbaceous plants which inhabit Tibet, Afghanistan, Turkestan, and the country from the Sea of Aral to the Persian Gulf. These are *Ferula Narthex* (Boissier) and *Ferula fœtida* (Regel). For drawings *v.* Bentl. a. Trim. 126–127, and Holmes (Pharm. J. [3] 19, 21, 41, and 365). Details of the mode of preparing the roots and of collecting the dried exudation are given by Flückiger and Hanbury (Flück. and Hanb. 316) and by Pereira (Mat. Med. 1853, 2, 1704). It is certain that asafœtida was known to the Arabian writers of the tenth century, and there is reason to believe that a knowledge of the drug is far more ancient.

Supplies of asafœtida are now almost entirely derived by way of India from Afghanistan. It occurs as tears more or less agglutinated, and sometimes as a honey-like mass. It is often largely mixed with earthy matter. When broken the milky white surface changes gradually to a pink, which passes into a brown hue (characteristic). Touched with nitric acid (sp.gr. 1·2) it gives a green colour. With water it forms an emulsion. The tears are brittle, and may be powdered when cold. Asafœtida has a powerful alliaceous odour and an acrid bitter alliaceous taste.

The chief constituents of asafœtida are *resin, gum,* and *volatile oil.* Their proportion varies with the age of the drug. For results of early investigations *v.* Gm. 17, 398. The resin is only partly soluble in ether and chloroform, but is entirely dissolved without alteration by concentrated nitric acid (*cf.* Johnston, Phil. Trans. 1840, 354). The U.S.P. demands that not less than 60 p.c., or, if powdered, not less than 50 p.c., shall dissolve in alcohol. The ash varies from 3–5 p.c. in pure 'tears' to 10 p.c. and higher in commercial 'mass.' For analyses and methods of assay, *see* Umney and Bunker (Pharm. J. 1910, 31, 147), Harrison and Self (*ibid.* 1912, 34, 205; 35, 139), Pearson (J. Ind. Eng. Chem. 1910, 2, 421). The use of the lead number is criticised by Rippetoe (Amer. J. Pharm. 1913, 199) and by Harrison and Self (Pharm. J. 1913, 36, 218). Hlasiwetz and Barth (Annalen, 138, 64) discovered in the resin *ferulic acid,* the methylphenolic ether of hydroxycinnamic or caffeic acid

$$C_6H_3(CH{:}CH{\cdot}COOH)(OCH_3)(OH)\,1:3:4$$

An alcoholic solution of asafœtida is precipitated by an alcoholic solution of lead acetate, and from the insoluble lead salt the ferulic acid is regenerated. It consists of needles melting at 168°–169° (Tiemann, Ber. 9, 416). Vanillin was shown to be present in asafœtida by Schmidt (Arch. Pharm. [3] 24, 534).

Pure drops of *Asafœtida amygdaloides* examined by Polásek (Arch. Pharm. 235, 125), gave the following, more or less typical, results: resin, soluble in ether, *asaresinotannol ferulate,* 61·40; resin, insoluble in ether, free *asaresinotannol,* 0·60; gum, 25·1; essential oil, 6·7; vanillin, 0·06; ferulic acid, 1·28; moisture, 2·36 p.c. On hydrolysis with potassium carbonate, the soluble resin yields asaresinotannol and ferulic acid; with sulphuric acid, however, it is hydrolysed into the same tannol and umbelliferone (for the latter compound, *see* under GALBANUM. Asaresinotannol is a brownish-yellow amorphous substance, and has the composition $C_{24}H_{34}O_5$.

When asafœtida resin is distilled alone, *variously tinted oils* are obtained, with ½ p.c. of umbelliferone (Sommer J. 1859, 573).

The gum of asafœtida consists of two portions, the one soluble and the other insoluble in water. The volatile oil is described by Flückiger and

Hanbury as of a light yellow colour with the odour of asafœtida. The taste is at first mild and then irritating, but it does not stimulate when applied to the skin like mustard oil. The oil is neutral, but becomes acid by exposure to the air, at the same time evolving sulphuretted hydrogen. Semmler (Ber. 1890, 23, 3530; 1891, 24, 78; especially Arch. Pharm. 1891, 229, 1) finds that it contains two *terpenes* $C_{10}H_{16}$ (together 6–8 p.c.); a *substance* $(C_{10}H_{16}O)x$ (20 p.c.), yielding with sodium a *sesquiterpene* $C_{15}H_{24}$ related to cadinene, a *disulphide* $C_7H_{14}S_2$ (45 p.c.), b.p. 80°–85°/9 mm., and a *disulphide* $C_{11}H_{20}S_2$ (20 p.c.), b.p. 120°–130°/9 mm. To the latter the odour is mainly due; on distillation under atmospheric pressure it decomposes with evolution of most repulsive smelling gases.

Asafœtida is used in medicine as a nervous stimulant and antispasmodic, and in the East as a condiment. In the United States it is extensively used in a disease of horses called 'heaves.'

Other varieties of asafœtida. The *Hing* used by the natives of Bombay is a variety of asafœtida. It is derived from *Ferula alliacea* (Boissier). It is more repulsive, and contains a larger proportion of volatile oil than asafœtida (Fluckiger, Pharm. J. [iii.] 6, 401; Fluck. a. Hanb. 319).

Bdellium.

Indian Bdellium; *False Myrrh*; *Bdellium.* This is the bdellium of the Bible, and is now used chiefly as an adulterant of myrrh. It is the product of *Balsamodendron Mukul* (Hooker) and, according to Dymock, also of the *B. Roxburgii* (Arnott) (*cf.* Pharm. J. [iii.] 6, 661; Holmes, *ibid.* 1898, 19, 547). Both are indigenous to India, but grow perhaps also in Southern Arabia. The gum-resin breaks with a flat conchoidal fracture, and though somewhat darker in colour, it resembles myrrh in appearance. It may be distinguished from myrrh by its not giving the violet colour reaction (*v.* *Myrrh*). (For analytical constants of bdellium *v.* Dieterich, Pharm. Centr. 40, 467.)

African Bdellium. A more highly esteemed bdellium, the product of *Balsamodendron africanum* (Arnott), a shrub indigenous to West Africa. It is used in France as a constituent of plasters. In fracture and other respects it resembles myrrh, but it does not give the violet colour reaction (*v.* *Myrrh*). African bdellium was analysed by Pelletier (Ann. Chim. Phys. [ii.] 80, 38), who found *resin* 59 p.c., *soluble gum* 9·2 p.c., *insoluble gum* 30·6 p.c., *volatile oil* and loss 1·2 p.c. The resin was further examined by Johnston (Phil. Trans. 1840, 368). *Cf.* Bley and Diesel (Arch. Pharm. [ii.] 43, 304).

Euphorbium. *Gomme-résine d'Euphorbe*, Fr.; *Euphorbium*, Ger. This extremely acrid drug has been known since the time of Dioscorides, but is now seldom employed in human medicine. It is the inspissated milky juice of *Euphorbia resinifera* (Berg), a cactus-like plant inhabiting Morocco and neighbouring districts of Northern Africa. A drawing is given by Bentl. a. Trim. 240. Euphorbium consists of irregular masses of a waxy-yellow or brown appearance, often inclosing spines and other fragments of the plant. It has a slight aromatic odour and an extremely acrid taste, its dust causing violent and even dangerous irritation to the nose or throat.

Flückiger (Flück. and Hanb. 560) found a selected specimen to consist of *amorphous resin*, 38 p.c.; *euphorbon*, 22 p.c.; *mucilage*, 18 p.c.; *malates of calcium, sodium,* &c., 12 p.c.; *mineral compounds*, 10 p.c. It contains no volatile oil.

Tschirch and Paul (Arch. Pharm. 234, 249) found, in addition to amorphous substances, 25 p.c. of malates and 40 p.c. of a crystalline substance, *euphorbon*, m.p. 115°–116°, to which they gave the formula $C_{30}H_{48}O$, but which has received three other formulæ from other investigators. It appears to be related to cholesterol.

When a filtered light petroleum extract of euphorbium resin is floated on a solution of one drop of concentrated sulphuric acid in 20 c.c. of water, a very stable blood-red layer is formed at the surface where the two liquids touch; on shaking, the whole of the acid liquid becomes red, and this colour only slowly changes to brown. This reaction may be used for purpose of identification; an extract of the most suitable concentration is obtained from 0·1 gram of euphorbium and 10 c.c. of light petroleum.

Euphorbium is now used mainly in veterinary medicine. Applied externally to the human subject it is irritant and vesicating, and internally administered it causes violent vomiting and purging. It is said to be an efficient preservative of iron and steel against corrosion (Year Book Pharm. 1880, 344).

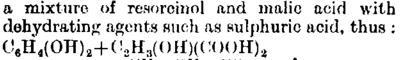
Power and Browning (Pharm. J. 1913, 36, 506) examined *Euphorbia pilulifera* from Fiji and isolated a number of crystalline alcohols and phenols, but no physiologically active substance. Von Wiesner (Monatsh. 1912, 33, 461) found that the latex of *E. lactiflora* from Chile contains 3·88 p.c. rubber and 28·3 p.c. resin. This low rubber and high resin content is characteristic of the latex of other species, which always contains also some euphorbon $C_{15}H_{24}O$.

Galbanum. *Gummi-resina Galbanum. Galbanum*, Fr.; *Mutterharz, Galbanumharz*, Ger. Galbanum has entered into the constitution of incense, and has been employed in medicine from the earliest times. It was used by the Israelites, and was well known to Hippocrates, Theophrastus, and Dioscorides, also to the Arabians, but has now disappeared from the British and United States pharmacopœias. Notwithstanding its antiquity, the precise plant from which galbanum is derived still remains uncertain. It is most probably obtained from the *Ferula galbaniflua* (Boissier and Buhse), and perhaps from other allied species of *Ferula*, natives of Persia. For figure *v.* Bentl. a. Trim. 128 (*cf.* Holmes, Pharm. J. [iii.] 19, 365). Marsden (Pharm. J. 1915, 41, 356) gives an analysis of a Persian sample and concludes that it is not derived from *F. galbaniflua*. The commonest commercial and late B.P. variety is from the Levant.

The gum-resin occurs in commerce in drops or tears, usually adhering into solid masses. In colour it exhibits various shades of light yellowish-brown, sometimes tinted with green. The odour of galbanum is aromatic, and the taste unpleasant, bitter, and alliaceous. Flückiger and Hanbury (Flück. a. Hanb. 323) note that when galbanum is warmed with concentrated hydrochloric acid a red colour is developed, which on the careful addition of spirit of wine, turns violet or bluish. Asafœtida treated in the same manner assumes a dingy colour, whilst ammoniacum gives no colour change at all. Further details of the characters of galbanum and its behaviour towards reagents are given in an elaborate memoir by Hirschsohn (Pharm. Zeit. 1875, 225; Pharm. J. [iii.] 7, 369, 389, 429, 531, and 571).

Galbanum resin examined by Conrady (Arch. Pharm. 232, 98) was found to contain 9·5 p.c. of ethereal oil; 63·5 p.c. of a resin soluble in alcohol; and 27·0 p.c. of impurities and gum. The pure resin obtained from the commercial product by extraction with alcohol and subsequent treatment with sodium salicylate contains 20 p.c. of combined umbelliferone; 50 p.c. of galbaresinotannol; and 0·25 p.c. of free umbelliferone. The resin which most probably consists of a galbaresinotannylic ester of umbelliferone is best hydrolysed by boiling with moderately diluted sulphuric acid since umbelliferone is unattacked by this reagent. *Galbaresinotannol* on analysis gives numbers agreeing with the formula $C_{18}H_{30}O_3$: on distillation with phosphoric anhydride it yields a hydrocarbon $C_{15}H_{20}$ and, on oxidation with nitric acid, camphoric and camphoronic acids. The volatile oil is obtained by distillation with water or by extraction with light petroleum. According to Fluckiger and Hanbury, the crude oil possesses an aromatic taste and is dextrorotatory On the addition of bromine to the oil extracted from Persian galbanum a red to violet or blue colour appears. The oil D 0·910–0·930 consists of *terpenes*, *d-pinene*, *nopinene*, *camphene*, and *myrcene*, of the sesquiterpene *cadinene*, of a substance $C_{10}H_{16}O$, and of the sesquiterpene alcohol *cadinol* $C_{15}H_{26}O$. (Semmler and Jonas, Ber. 1914, 47, 2068, where the older literature is given.) Cadinol is a new substance.

When galbanum resin is distilled a small quantity of umbelliferone is obtained (Sommer, J. 1859, 573). This compound is now known to be a product of the distillation of many other resins or gum-resins, especially those of the *Umbelliferæ*. Galbanum yields 0·83 p c., sagapenum 0·32 p.c., asafœtida 0·28 p.c. Synthetically, umbelliferone may be produced, as pointed out by Pechmann (Ber. 17, 932), by acting upon a mixture of resorcinol and malic acid with dehydrating agents such as sulphuric acid, thus:



$$C_6H_4(OH)_2+C_2H_3(OH)(COOH)_2$$
$$=C_6H_3(OH)<\begin{array}{l}CH=CH-CO\\O\end{array}+HCOOH+2H_2O$$

Another product of the destructive distillation of galbanum resin is a thick *brilliant blue oil.* The oil deposits in the cold crystals of umbelliferone. It has a bitter acrid taste and aromatic odour. Kachler (Ber. 4, 36) separated it into a *colourless hydrocarbon* $C_{10}H_{16}$ boiling at 240°, and a *blue oil* $C_{10}H_{16}O$ which boiled at 289°. The flowers of the wild chamomile *Matricaria Chamomilla* (Linn.) yield a blue oil very similar to that obtained from galbanum. Both oils are converted by potassium into the hydrocarbon $C_{10}H_{16}$, which on the addition of bromine vapour gives the blue colour reaction. Hlasiwetz and Barth (Annalen, 130, 354) have shown that by fusing galbanum resin with potash as much as 6 p.c. of resorcinol is formed (*cf.* Goldschmied, Ber. 11, 850); and by treatment with nitric acid, Will and Boettger (Annalen, 58, 269) obtained styphnic acid (*cf.* Schwanert, Annalen, 128, 123).

Galbanum is administered in medicine internally as an expectorant, and externally it is applied in the form of plasters.

A table of the acidity, ether, and saponification numbers of galbanum resin is given by Dieterich (Pharm. Centh. 40, 467).

Gamboge. *Cambogia*, U.S.P.; deleted from B.P. in 1914. *Cadie Gum*, *Gummi Gambogia*, *Gummi Gutti*, *Gomme Gutte*, Fr.; *Gutti*, *Gummigutt*, Ger. This beautiful orange-red gum-resin comes to us from Camboja, Siam, and Cochin China, where it is the product of a laurel-like tree, the *Garcinia Hanburyi* (Hook.); *v.* Bentl. a. Trim. 33. Indian gambogo is obtained from *G. Morella* (Desrouss.) Gambogo was known to the Chinese in the thirteenth century, but it was not until the seventeenth century that it appeared in European markets. For the purpose of collecting it the trees are incised, and sections of bamboo are attached to collect the milky juice, which, hardening by evaporation, takes the cylindrical shape of the receiving vessel. Gamboge as it occurs in commerce is brittle, and may be powdered readily. In presence of water it forms at once a yellow emulsion. It has a disagreeable and acrid taste.

Costelo (Amer. J. Pharm. 1879, 174) finds the *resin* to vary from 68 to 79 p.c., and the *gum* from 19 to 27 p.c. (*cf.* Hurst, Pharm. J. [iii.] 19, 761). The gum is extracted by water. Its solution, like arabic, is not precipitated by neutral lead acetate, but its behaviour towards other reagents shows it to be a different gum.

Alcohol dissolves the resin. By fusion with potash, Hlasiwetz and Barth (Annalen, 138, 68) obtained phloroglucinol, pyrotartaric, isouvitic, and various fatty acids.

For the detection of gamboge in mixtures, *v.* Hirschsohn (Pharm. Zeit. 24, 609). The material is ground up with hydrochloric acid, when ether extracts a yellow colouring matter, soluble in dilute ammonia with an orange colour. In medicine gamboge is employed as a drastic purgative, usually in combination with other substances. It is also an important water colour.

Ivy gum resin. *Gummi-resina Hederæ.* In Southern Europe and in the Levant a gum-resin is obtained from the old trunks of the common ivy, *Hedera Helix* (Linn.). It consists of irregular masses of a reddish or yellowish-brown colour externally, but showing a deep red by transmitted light. The taste is bitter and acrid, but when heated it evolves a balsamic odour. Pelletier (Bull. Pharm. 4, 504) found the gum-resin to consist of *resin* 23 p.c., *gum* 7 p.c., and 70 p.c. of woody fibre. Examined by Sommer (Arch. Pharm. [ii.] 98, 11) it gave no umbelliferone.

Myrrh. *Myrrha*, B.P.; U.S.P.; *Herabol Myrrh*; *Gummiresina Myrrha.* *Myrrhe*, Fr.; *Myrrhe*, Ger. Together with olibanum, myrrh has been used as a constituent of incense from the earliest times. It is mentioned in Genesis and in other places in the Bible. The Egyptians employed it not only in fumigations, but also in embalming and in medicine. It has retained its place down to the present day, and is included in all the pharmacopœias. Myrrh is the spontaneous gum-resinous exudate of the shrubs or small trees of the *Balsamodendron Myrrha* (Nees)=*Commiphora Myrrha* (Holmes), an inhabitant of the Somali coast of the Gulf of Aden and of the Red Sea coast of Arabia (Trimen, Pharm. J. [iii.] 9, 893). A drawing of the tree is given by Bentl. a. Trim. 60. The exudate is allowed to harden on the tree before collection. It occurs in irregular-shaped masses of a red-brown colour and dusty appearance. When cold it is brittle, and breaks with an uneven, waxy, oily-looking fracture, often exhibiting lighter-coloured semicircular striations. With water it readily yields an emulsion. The odour of myrrh is fragrant and agreeable, and the taste bitter, aromatic and acrid.

The chief constituents of myrrh are *gum*, *resin*, and *volatile oil*. The relative proportions, even in the case of true myrrh, vary greatly in different specimens. Generally the gum constitutes 40–65 p.c., the resin 25–40 p.c., and the volatile oil 2·5–8 p.c. Fluckiger and Hanbury (Flück. a. Hanb. 143) found 27 p.c. of resin in a good specimen, and Kohler (Arch. Pharm. 228, 291) found 7–8 p.c. of volatile oil. Brückner's analysis (Neues Rep. Pharm. 16, 76) gave: soluble in water, gum, 67·76 p.c.; resin soluble in carbon disulphide, 14·06 p.c.; resin soluble in ether, 12·57 p.c.; resin insoluble in ether, 4·81 p.c.; substances soluble in diluted alcohol, 0·43 p.c.; insoluble (sand, bark, &c.), 0·38 p.c. The U.S.P. demands that at least 35 p.c. shall be soluble in alcohol, and that the ash shall not exceed 8·5 p.c.

Myrrh resin is soluble in alcohol or chloroform, but it is only partly soluble in ether, carbon disulphide, or alkalis. According to Köhler (*l.c.*) it is a mixture of several resins, the greater portion of which is a soft resin $C_{26}H_{34}O_5$ soluble in ether. There are also present two dibasic acids $C_{13}H_{16}O_{18}$ and $C_{26}H_{32}O_9$ respectively.

Tschirch and Bergmann (Arch. Pharm. 1905, 243, 641) have made an examination of so-called Myrrha electa, which is the true or Herabol myrrh obtained by sorting from the other resins (Indian and African bdellium, Bisabol myrrh, Opoponax) mixed with which myrrh is imported into the United Kingdom. Holmes (Pharm. J. 1913, 37, 116), in describing Somali myrrh, disputes this, and maintains that it is derived from *Balsamodendron Myrrha*. Tschirch and Bergmann (*l.c.*,) and Friedrichs (Arch. Pharm. 1907, 245, 427) have described a large number of amorphous constituents, but the chemistry of myrrh abounds in contradictions, perhaps owing to difference in origin of the material examined (*cf.* Greenish, Pharm. J. 1901, 67, 666).

Myrrh resin gives a violet colour when a fragment moistened with alcohol is treated with nitric acid, or the ethereal extract is treated with bromine vapour. It is best to dilute the alcoholic extract with water, shake out with light petroleum, and treat the residue after evaporating the petrol, with nitric acid. The colour is not so marked as in the case of galbanum (*cf.* Ruickholdt, Arch. Pharm. [ii.] 41, 1; Held, Annalen, 63, 59; Hager, Pharm. Centh, 1865, 58). Bdellium (*q.v.*), also derived from *Balsamodendron* species, is somewhat similar to myrrh, but does not give this colour reaction. Distilled, myrrh gives no umbelliferone, but by fusion with potash Hlasiwetz and Barth (Annalen, 139, 78) obtained small quantities of catechol and protocatechuic acid. The property of giving a violet colour when oxidised by nitric acid, or better, by bromine vapour, is confined to that resin which dissolves in carbon disulphide, and which, according to Brückner, contains 75·6 p.c. of carbon.

The gum of myrrh on analysis gives numbers agreeing with the formula $C_6H_{10}O_5$. On treatment with hydrochloric acid it yields lævulic acid (Kohler). It contains an oxydase (Tschirch and Bergmann von Friedrichs).

The quantity of volatile oil in myrrh varies very greatly. Gladstone (Chem. Soc. Trans. 17, 11) describes it as a viscid brownish-green oil that, boiling at 266°, gives an oxidised product. Its sp.gr. was 1·0189. The oil prepared by Flückiger (*cf.* Ber. 9, 471) was lighter than water, the sp.gr. at 13° being 0·988, and the boiling-point 270°–290°. Redistilled in a current of carbon dioxide it passed over between 262° and 263°. After redistillation the oil, on addition of a drop of nitric acid, gave after an hour or two a permanent violet hue, but this is better observed when bromine vapour is applied to a solution of the crude oil in carbon disulphide.

Samples of the oil examined by Lewinsohn (Arch. Pharm. 1906, 244, 412) contained cuminaldehyde up to 1 p.c. and small quantities of eugenol and *m*-cresol, and of acetic and palmitic acids. By distillation over sodium, pinene, dipentene, and limonene were isolated, and in one commercial sample, a fourth *terpene* $C_{10}H_{16}$, b.p. 78°–80° (20 mm.). Two other possibly new *sesquiterpenes* $C_{15}H_{24}$, b.p. 151°–154° (15 mm.) and b.p. 163°–168° (12 mm.) respectively, were obtained from two other samples of the oil. Von Friedrichs (*l.c.*) obtained from the essential oil, formic and acetic acids; a crystalline *acid*, m.p. 159°; *m*-cresol; cuminaldehyde and cinnamaldehyde; crystalline monobasic *myrrholic acid* $C_{17}H_{22}O_5$, m.p. 236°; and the sesquiterpene *herabolene* $C_{15}H_{24}$, b.p. 130°–136° (16 mm.).

According to Flückiger, the *bitter constituent* of myrrh is a glucoside. V. Bolton (Zeitsch. Elektrochem. 14, 211), by extracting myrrh with alcohol, evaporating to dryness and then extracting with water, obtained a substance *burseracin*, which forms 1·5–2 p.c. of the original drug. It is a yellow hygroscopic powder, m.p. 78°, and has the composition $C_{20}H_{28}O_8$. It is not a glucoside. On treatment with hydrogen peroxide a compound is obtained, which appears to be radioactive.

Myrrh is a reputed stimulant and tonic, but its employment in medicine depends chiefly on its aromatic properties.

Other varieties of myrrh. Several gum-resins more or less resembling true myrrh are occasionally found in commerce. Two are described by Flückiger and Hanbury. One of these, often incorrectly called *East Indian myrrh*, but which is really an African drug, is known as *bisabol* or *hebbakhade*. In outward appearance it is very similar to true myrrh, but it is more acrid, and its resin, soluble in carbon disulphide, gives no violet colour with bromine vapour. An analysis of bisabol-myrrh from

Somaliland gave the following results: gum soluble in water, 22·1; gum soluble in soda, 29·85; resin, 21·5; bitter principles, 1·5; volatile oil, 7·8; water, 3·17; and inorganic matter, &c., 13·4 p.c. (Tucholka, Arch. Pharm. 235, 289).

The other variety is *Arabian myrrh*. It is collected in Southern Arabia east of Aden, and is probably the product of a distinct species (Hanbury). It is very nearly related to true myrrh in appearance, and some specimens give the violet colour reaction.

Olibanum. *Frankincense*; *Gummi-resina Olibanum*; *Thus masculum*. *Encens*, Fr.; *Weihrauch*, Ger. Olibanum or frankincense has been the favourite basis of incense from the earliest times. It is frequently referred to in the Bible, and the Egyptians employed it for fumigations and for embalming.

Duemichen, in his book on the Paintings of the Temple of Dayr el Báhri in Upper Egypt, which represent the traffic between Egypt and a land called Punt as early as the seventeenth century B.C., has shown that these paintings include, not only representations of olibanum in bags, but boxes or tubs containing living olibanum trees. Tribute offerings of frankincense were common throughout the ancient world. At the present day the incense of the Roman and Greek Churches is largely composed of olibanum.

The gum-resin is the dried exudated juice of several species of *Boswellia*. These trees, the fragrance of which is noticeable even at a distance, inhabit Eastern Africa, near Cape Gardafui, and the southern coast of Arabia. They were studied by Birdwood (Trans. Linn. Soc. 27, 111, 148). One of them is figured by Bentl. and Trim. 58 (Flück. a. Hanb. 134). Olibanum is a solid which softens in the mouth, and has a slightly terebinthinous, not disagreeable, taste. It consists of tears of various shapes, generally detached. The odour, especially on heating, is pleasantly aromatic. It has a pale yellow or brown colour, and the larger fragments are more or less milky and translucent. Triturated with cold water it yields an emulsion.

The chief constituents of frankincense are *resin, gum*, and *volatile oil*. The oil is obtained by distillation; alcohol dissolves the resin and water the gum. Braconnot (Ann. Chim. Phys. [i.] 68, 60) found resin 56 p.c., soluble gum 30 p.c., insoluble gum 6 p.c., and volatile oil 8 p.c.; whilst the analysis of Kurbatow gave resin 72 p.c., gum 21 p.c., and volatile oil 7 p.c (Zeitsch. Chem. [ii.] 7, 201). From the resin Tschirch and Halbey (Arch. Pharm. 236, 487) obtained *boswellic acid* $C_{32}H_{52}O_4$, a white powder, m.p. 150°, which shows little tendency to crystallise. The resin probably contains boswellic acid in the form of an ethereal salt, and also *olibano-resene* $(C_{14}H_{22}O)_n$, a powder insoluble in sodium hydroxide and melting at 62°. According to Kurbatow, an *oil* boiling at 360° is obtained when the resin is subjected to destructive distillation. No umbelliferone is obtained (Sommer, J. 1859, 573).

The gum of olibanum behaves towards reagents exactly as gum arabic (Heckmeijer, J. 1858, 482).

Volatile oil of olibanum examined by Stenhouse (Annalen, 35, 308) gave the following data (Schimmel & Co., Semi-Annual Report, April, 1914) D^{15} 0·8775, a_D+19° 18′, n_D^{20} 1·47245, acid number 1·8, ester number 7·5, ester number after acetylation 106·0. The sample dissolved in 2 vols. or less of 90 p.c. alcohol, but became turbid on addition of a further quantity. The terpene fraction consisted mainly (99 p.c.) of α-pinene and camphene, with a little dipentene and cymene, but no phellandrene. Formerly commercial samples were lævorotatory, but are now generally dextrorotatory. Fromm and Autin (Annalen, 1913, 401, 253) found for the oil freed from terpenes, b.p. 70°/12 mm. D^{15} 0·9685, a_D+20° 48′ and separated it into a small fraction b.p. about 150°, two main fractions b.p. 210°–211° and 260° and a viscous residue. The fraction b.p. 210°–211° contains a substance *olibanol*, $C_{10}H_{16}O$ which is not an ether; its constitution is discussed. The same name was given by Haensel (Chem. Zentr. 1908, i, 1837) to an alcohol $C_{26}H_{44}O$, b.p. 333°–334° from oil of frankincense with $D^{17.5}$ 0·8810, a_D+22·08°, acid number 2, ester number 15·5. At the present day olibanum is seldom employed in medicine. It is used almost exclusively in the preparation of incense.

Opopanax. A bright orange-brown gum-resin occurring in hard nodular or earthy-looking lumps. It was used by Hippocrates, and several varieties were known to Theophrastus and Dioscorides. It is said to be derived from the *Opopanax Chironium* (Koch), a native of Southern Europe.

Opopanax consists essentially of *resin, gum*, and a little *volatile oil*. The most recent examination of opopanax is that by Tschirch and Knitl (Arch. Pharm. 237, 256), who found a specimen from the *Opopanax Chironium* (Koch) to contain: resin soluble in ether 51·8, resin insoluble in ether 1·90, gum 33·8, volatile oil 8·3, free ferulic acid 0·22, vanillin 0·0027, moisture 2·0, bassorin and plant remains 2·0 p.c. The resin soluble in ether is the ferulate of a resinotannol, and on hydrolysis ferulic acid and *oporesinotannol* are obtained. The latter is a light brown powder having the composition $C_{12}H_{13}O_2(OH)$. The resin of opopanax insoluble in ether consists of free oporesinotannol. The purified gum contained 3·53 p.c. of ash, and an arabic acid was prepared from it containing C 43·17, H 6·42 p.c. From the volatile oil a product was obtained in needles, which melted at 133°–134° and had the composition C 66·6, H 2·7 p.c. This substance is named *oponal*.

A sample of opopanax examined by Baur (Arch. Pharm. 233, 209) contained plant fragments which showed it to be derived from some member of the genus ***Balsamodendron***, order *Burseraceæ*, probably from *B.* ***Kafal*** [***Commiphora*** *abyssinica* (Engl.)]. It contained 19 parts p.c. of resin, 6·5 of ethereal oil, and 70 of gum, besides plant fragments.

The resin of opopanax gives no umbelliferone when distilled. When fused with potash, Hlasiwetz and Barth found the resin to yield catechol, together with protocatechuic acid (Annalen, 139, 78). The substance formerly known by the name of opopanax was altogether resin described above. It was probably derived from a Persian member of the *Umbelliferæ* (Powell, Economic Products of the Punjab, 1, 402; Flück. a. Hanb. 327). This resin differs from the usual variety by yielding umbelliferone on dry distillation, also the volatile oil obtained from it contains sulphur.

Opopanax was highly esteemed in ancient medicine, but it has now gone entirely out of use.

Sagapenum. This gum-resin, which, like galbanum and asafœtida, has been known from the earliest times, is now seldom met with. Its botanical origin is not known with certainty. Flückiger and Hanbury (Flück. a. Hanb. 324) describe sagapenum as consisting of a tough, softish mass of closely agglutinated tears. The tears are brownish, not milkwhite like asafœtida, and when broken do not acquire a pink tint, and are without alliaceous odour. The specimen of sagapenum examined by these observers contained no sulphur, but yielded umbelliferone. Seven out of the eight specimens examined by Hirschsohn (Pharm. Zeit. 1875, 225; Pharm. J. [iii.] 7, 771), however, contained sulphur, and this character served to distinguish sagapenum from ammoniacum, galbanum, and opopanax. Umbelliferone was always obtained. Unlike galbanum, sagapenum dissolves in light petroleum; it further contains a much larger proportion of resin. When some specimens of sagapenum are immersed in hydrochloric acid (sp.gr. 1·13) they acquire a permanent blue colour, but others do not exhibit this behaviour.

A specimen of sagapenum investigated by Hohenadel (Arch. Pharm. 233, 259) was found on examination of the plant fragments contained in the drug to have been obtained from the stems and fruits of a Persian species of *Ferula*, order *Umbelliferæ*. It contained resin, 56·8; volatile oil, 5·8; water, 3·5; gum, 23·3; and impurities, 10·6 p.c. The purified resin is yellowish-brown, and melts at 74°–76°; when hydrolysed by boiling with sulphuric acid it is decomposed into umbelliferone and *sagaresinotannol*, a brown substance having the composition $C_{24}H_{28}O_5$. The 56·8 parts of purified resin contained 40 of sagaresinotannol, 15·7 of combined, and 0·11–0·15 of free umbelliferone. The ethereal oil contains 9·7 p.c. of sulphur.

Scammony. *Scammonée*, Fr.; *Scammonium*, Ger. A purgative gum-resin derived from the *Convolvulus Scammonia* (Linn.), a native of Greece, Asia Minor, Syria, and Southern Russia.

The gum resin obtained by incision from the living root, and known as scammony or 'virgin scammony,' has been used medicinally for many centuries, but was deleted from the B.P. in 1914, and from the U.S.P. in 1916. The value of this drug depends on its resinous constituent, which, however, is now usually prepared by extracting the dried scammony root with alcohol, and precipitating the resin from the solution with water; but the resin from both of these sources appears to have been displaced in the market, to a large extent, by the resin obtained from the root of *Ipomoea orizabensis* (Ledanois), commonly known as 'Mexican scammony root,' and until lately these two resins have usually been considered to be chemically identical. The B.P. now has *Scammoniæ resina*, *Scammoniæ radix* (from *Convolvulus Scammonia L.*) and *Ipomœa* (Mexican Scammony, the root of *I. orizabensis*, added 1914) the U.S.P. now has *Resina Scammoniæ* and *Scammoniæ radix* (root of *C. Scammonia L.*, yielding 8 p.c. resin, added 1916).

An investigation of scammony root and scammony made by Power and Rogerson (Chem. Soc. Trans. 1912, 101, 398) shows that the resins obtained from the root by the methods of incision and extraction, although similar, are not identical, while both these resins differ very considerably from that obtained from the root of *Ipomoea orizabensis*, which has also been examined by Power and Rogerson (*ibid.* 101, 1). Both of these resins are exceedingly complex in character, but consist to a large extent of glucosides and methylpentosides of jalapinolic acid and its methyl ester, and, whilst the methylpentose obtained by the hydrolysis of the resin of scammony root appears to be identical with rhamnose, that from the resin of *Ipomoea orizabensis* yields a crystalline tetra-acetyl derivative not hitherto described. The resin from the last-mentioned source also contains small proportions of hentriacontane and cetyl alcohol, which are not present in the resin from scammony root; also, differences are observed in extracting with various solvents both the crude resins and the products of their alkaline hydrolysis. In particular the true resin is almost completely soluble in ether (the U.S.P. demands that at least 95 p.c. should dissolve) whereas of Mexican scammony only about 70 p.c. is soluble.

According to Scoville (J. Ind. Eng. Chem. 1919, ii., 335) several botanical species, closely allied, furnish scammony or scammony substitutes, among them, a Mexican plant, *Resina drastica*.

Jalapinolic acid $C_{15}H_{30}(OH)CO_2H$ was first obtained by Mayer (Annalen, 95, 149) from 'jalapin,' the name given to that portion of the resin of *Ipomoea orizabensis*, which is soluble in ether. Jalapinolic acid, subsequently investigated by Kromer (J. pr. Chem. [ii.] 57, 448), has been studied by Power and Rogerson (*l.c.*). It forms silky needles, m.p. 67°–68°, and is slightly dextrorotatory. The *methyl ester* boils at 220° (20 mm.) and crystallises in laminæ, which melt at 47°–48°.

For an account of the characteristics of scammony resin, its substitutes and adulterants, *see* also Bourdier (J. Pharm. Chim. 1912, 5, 251). The microscopic differences between true and Mexican scammony, together with some colour reactions, are given by Ballard (Pharm. J. 1912, 34, 285). For the earlier investigations on scammony resin and on the sugars obtained by its hydrolysis *see* the above-quoted papers by Power and Rogerson, and their paper in J. Amer. Chem. Soc. 32, 112. G. B.

GUMS. Gums are amorphous substances, composed of carbon, hydrogen, and oxygen, which are characterised by the property of either dissolving in water, or of taking up enough of that solvent to become glutinous and form a mucilage. They are either derived from plants by spontaneous exudation, or are extracted by means of solvents. The gum usually contains some inorganic matter and occasionally a small proportion of nitrogen (*cf.* Stevens, Amer. J. Pharm. 77, 255). For a long time the gums were considered to be carbohydrates. It is now known, however, from the researches of O'Sullivan on gum arabic (Chem. Soc. Trans. 45, 41; 57, 59), Gedda gum (*ibid.* 59, 1029), and gum tragacanth (*ibid.* 79, 1164), that the gums are acids of high molecular weight, composed of an acid nucleus to which is attached a number of residues of various hexoses, pentoses, and bioses by means of ethereal oxygen linkings; the principal sugars obtained in hydrolysis are galactose and arabinose.

The proportions of the sugars united to the nucleus acid to form the natural complex gum acid, and the proportions of the complex acids in the mixture that constitute the natural gum, appear to vary in different seasons, since investigations have shown that the properties of the gum of a given plant are not always the same.

The finer gums are used in pharmacy in the preparation of emulsions and pastilles, and as a constituent of emollient medicines, whilst the commoner qualities are used in the arts as adhesive agents, in the finishing of cloth, in the preparation of ink, of water colours, and in calico printing.

Many drugs, known as gums in commerce and not included in this article, will be found by reference to BALSAMS or GUM RESINS.

One of the most important factors in determining the quality of a gum is the viscosity of the solution it forms with water, and as no standard method is yet in use the results recorded by different investigators are usually not comparable. The simplest method of determining the viscosity is to allow a quantity of the solution (say of 10 p.c.) to flow by its own weight out of a tube, provided with a capillary orifice, and to note the time of flow. The results obtained by this method are of little value, since the pressure under which the liquid flows varies continuously, but the method is still in use as affording a rough comparison of viscosities. For more accurate work, recourse may be had to the use of a viscometer, such as that described by Ostwald (Physico-Chemical Measurements, 162).

In addition to the viscosity determination, it is generally necessary to ascertain the percentage of moisture present in a sample of gum, the acidity, the amount of ash, the colour, taste, odour, and character of the solution it forms with water. The amount of moisture present should be merely enough to prevent the gum being excessively friable; as a rule it varies between 12 and 16 p.c. The ash should be merely that due to the bases combined with the natural gum acid and in good samples is generally about 3 p.c. The solution should be free from marked taste or odour and not very dark in colour.

In the early part of the 19th century, a good many gums were known, and the work then done resulted in the description of the properties of a few gum substances to which the names *bassorin*, *cerasin*, and *arabin* were given; and chemists, dominated by the idea that the number of organic compounds was only small, on investigating a gum, identified its constituents with one or more of these substances. It now appears that the number of gum compounds is very considerable, and it cannot be safely inferred that the arabin, or cerasin, &c., found in one gum, is the same substance as the compound, given the same name, found in another natural product. For further particulars, *see* Robinson (Brit. Assoc. Reports, 1906, 227; and the Imperial Institute Bulletin, 6, 29), from which much of the information embodied in this article has been obtained.

ACACIA AND ALLIED GUMS.

Acacia gum. *Gum arabic*; *Acaciæ gummi*, B.P.; *Acacia*, U.S.P.; *Gomme arabique*, Fr.; *Arabisches Gummi*, Ger. Acacia gum is the exudation from the stems and branches of various species of acacia, notably the *A. Senegal* (Willd.), which inhabit Africa from Senegambia in the West to Kordofan, Southern Nubia, and the region of the Atbara in the East (Bentl. a. Trim. 94; Höhnel, Pharm. J. [iii.] 18, 1089; Fluck. a. Hanb. 233). The drug has been known from the earliest times, having been an article of Egyptian commerce in the 17th century B.C.

The most esteemed variety is *Picked Turkey* or *white Senaar gum*. This gum, also known as *Sudan or Kordofan gum*, is collected from the grey barked acacia tree, *Acacia Senegal* (Willd.), known locally as 'hashab.' In Kordofan, the gum is obtained both from gardens of acacia trees which are private property and from wild trees. In the gardens, the gum is obtained by artificially incising the trees soon after the end of the rainy season, the bark is removed in strips from the principal branches of all trees which are three years old or upwards; the strips should be 1 to 3 inches wide, according to the size of the branch, and 2 to 3 feet in length. The incision should not penetrate into the wood, and a thin layer of the inner bark should be left. About 60 days afterwards, the first collection of gum is made, and after that the gum is collected every fourth day until the rains recommence and new leaves appear; at this stage the exudation ceases. The gum obtained from the wild or uncultivated trees is slightly darker in colour and of less value than that derived from trees under cultivation. It exudes naturally from the wild trees and usually dries into pear-shaped pieces which vary in size, according to the length of time between successive collections. Young hashab trees, 8 to 10 feet high and 6 to 8 inches in girth, will produce gum, and the limits of age for this purpose may be taken as 3 to 15 or 20 years; probably trees of from 8 to 12 years old are the most productive. The gum consists of lumps of various sizes, sometimes as large as a walnut, and of a white or nearly white colour. The unbroken masses are rounded in shape, and traversed by numerous minute fissures. They are brittle and break with a vitreous fracture, exposing a transparent and in the finer varieties quite colourless interior.

Suakin, Talca, or Talha gum is derived from the 'red' and the 'white' barked acacia trees, both of which are varieties of *Acacia Seyal* (Delile). It is collected chiefly in the forests of the Blue Nile. The red talha tree is more abundant than the white and consequently most of the talha gum is derived from that variety. The trees are said not to be barked or wounded by the collectors, who gather the gum they find exuding. Talha gum is so brittle that commercial specimens have usually, for the most part, fallen to powder. The particles exhibit a great variety of colour.

Senegal gum, collected in the French colony of Senegal, is obtained almost entirely from the same species of acacia which yields the Kordofan gum, but it is probable that the poorer qualities are procured from other species. The gum exudes naturally through fissures produced by the rapid and unequal desiccation of the barks of the trees by the hot winds experienced immediately after the wet season, but in recent years incisions have been made. Senegal gum is much darker in colour than the Sudan gum, and the surface of the lumps is unbroken by cracks or fissures. It is chiefly imported into France. A considerable quantity of this is however, exported to other European countries.

Morocco, Mogador, or **Brown Barbary gum** is exported from Morocco. It is stated to be obtained from *Acacia arabica* (Willd.), and *Acacia gummifera* (Willd.), but according to some authorities, much of the gum now exported is merely Senegal or Sudanese gum, brought to Morocco by caravans from the interior. It consists of light dusky brown tears or vermiform pieces; they show numerous superficial fissures.

Cape gum is the product of the *Acacia horrida* (Willd.), a native of Cape Colony. Its colour is amber-brown.

Aden and **East Indian gum** is produced in Abyssinia and Somaliland and is exported from the towns on the Somali coast principally to Aden and Bombay. From these two ports, it is reshipped to Europe as 'Aden gum' and 'East Indian gum' respectively. The source of the gum is not known with certainty but some of it is doubtless collected from *Acacia abyssinicia* (Hochst.) and *Acacia glaucophylla* (Steud.), which are known to occur in those regions. It consists of tear-shaped masses, often as large as an egg, and of a pale amber or pinkish hue. The best qualities approach the better classes of Kordofan gums in appearance, solubility, and other characters, but these gums are usually darker in colour.

Australian or **Wattle gum**, the product of several Australian species of Acacia known locally as 'Wattles,' occurs in large hard globular tear-like masses or lumps, varying in colour from deep yellow to deep reddish-brown (*v.* Maiden, Pharm. J. [iii.] 20, 86; *cf.* Flück. a. Hanb.).

Gum arabic is not much more soluble in hot than in cold water. In alcohol it is insoluble. The aqueous solution is precipitated by basic lead acetate, but not by neutral acetate; 10 c.c. of a 10 p.c. solution gives a precipitate with 0·1 c.c. of basic lead acetate solution (U.S.P.). It is also thickened or rendered turbid by the addition of solutions of borates or ferric salts or alkaline silicates. Salts of mercury or silver have no action on the solution, neither is it coloured blue by iodine. Gum arabic yields about 3 p.c. of ash, consisting of calcium magnesium and potassium carbonates. For analytical distinctions between pure gum arabic and gums with which it may be associated, *v.* Hager (Zeitsch. anal. Chem. 11, 350; Pharm. Centh. 1885, 388); Schlosser (Chem. News, 20, 120); Roussin (J. Pharm. Chim. [iv.] 7, 251); Elwood (Pharm. J. [iii.] 19, 339); Hefelmann (Zeitsch. öffentl. Chem. 11, 195); Palladino (Bull. Soc. chim. [iii.] 9, 578); Vamvakus (Ann. Chim. anal. 12, 12). Methods of valuation of gum arabic are given by Fromm (Zeitsch. anal. Chem. 40, 143) and Dieterich (*ibid.* 40, 408).

Gum arabic contains an oxidase (*e.g.* Reinitzer, Zeitsch. physiol. Chem. 1909, 61, 352), tragacanth does not. Hence, when a drop of hydrogen peroxide is added to a mixture of equal volumes of a cold 1 : 30 aqueous gum solution and tincture of guiacum, a brown colour results with gum arabic; tragacanth remains colourless (Allen's Comm. Org. Analysis, 1911, vol. iv., p. 444).

Starch is detected by iodine; dextrin by a method due to Roussin (*l.c.* and Allen, *l.c.* p. 439); gelatin by tannic acid, *cf.* also Trillat (Compt. rend. 127, 724). The quantitative estimation is described by Waters and Tuttle (J. Ind. Eng. Chem. 1916, 8, 413). They precipitate with an ammoniacal copper acetate solution in 50 p.c. alcohol, wash the precipitate with alcohol, dry at 105°, weigh and subtract the copper oxide left on ignition.

The chief constituent of gum arabic is *Arabin, Arabic acid*, or *Gummic acid*, combined with calcium and also perhaps with magnesium and potassium. The crude acid is precipitated when alcohol is added to an aqueous solution of gum arabic previously acidified with hydrochloric acid. By successively redissolving in water and reprecipitating, the product can be obtained pure. Arabic acid is amorphous, soluble in water and insoluble in alcohol. Heated to 100° it is converted into insoluble *meta-arabic acid* (Neubauer, J. 1854, 624; Annalen, 102, 105; Gelis, J. 1857, 496), or the same change may be effected by treatment with concentrated acid (Fremy, J. 1860, 503). Meta-arabic acid is readily changed back again to soluble arabic acid by the action of alkalis. Heat of combustion, *v.* Stohmann (J. pr. Chem. [ii.] 31, 298). Action of light, *v.* Eder (*ibid.* 19, 299).

The constitution of arabin has been investigated by O'Sullivan (*l.c.*) who showed that it contains the acid nucleus, $C_{23}H_{38}O_{22}$, to which he gave the name *λ-arabinosic acid*, but afterwards unfortunately called it *arabic acid*, the name already given to the naturally occurring gum acid, arabin, which is a compound of arabinosic acid with the sugar residues, arabinan and galactan, the termination 'an' indicating the anhydride of the corresponding sugar. On complete hydrolysis, arabin yields arabinose, galactose, and arabinosic (arabic) acid.

When oxidised with ordinary nitric acid, gum arabic yields oxalic, mucic, tartaric, and racemic acids (Guerin, Annalen, 4, 255; Liebig, *ibid.* 113, 4; Kiliani, Ber. 15, 35; Hornemann, J. 1863, 391; Maumene, Bull. Soc. chim. [iii.] 9, 138; Béchamp, *ibid.* [iii.] 7, 587).

Gums from *Acacia pycnantha* (Australia), *A. horrida* (S. Africa), *A. arabica* (Africa, Arabia, India), and *Melia Azadirachta* (Deccan, Ceylon, Malay Archipelago) have been examined by Meininger (Arch. Pharm. 1910, 248, 171).

Allied gums. The gum known in commerce as *Gedda gum*, in appearance very similar to the inferior kinds of gum arabic, has also been examined by O'Sullivan. He found that it is a mixture of several gum acids, which are constituted of the radicles of galactose and of arabinose or arabinan, attached in considerable numbers to a nucleus acid to which the name geddic acid is given. Geddic acid is an isomeride of arabic acid, $C_{23}H_{38}O_{22}$. *Chagual gum* is obtained from Chile, where it is produced by the *Puza lanuginosa* (Schult.). It is partly insoluble in water. Chagual gum has been investigated by Winterstein (Ber. 31, 1571). *Feronia* or *wood apple gum* is derived from the Indian tree *Feronia elephantum* (Correa) (*cf.* Flück. a. Hanb. 239). *Ghati gum* is the name given in India to gum produced in India itself, as distinguished from East Indian gum of exotic origin. In European commerce, however, the name 'Ghatti' or 'Gatty' is practically restricted to the partially soluble and viscous gum derived from *Anogeissus latifolia* (Wall.) and certain other species. It is derived from various trees and no attempt is made to keep the products of the different species separate. The result of this is that the gum may differ considerably in properties. *Hog* or *Doctor gum* consists of reddish tears. It is derived from the *Rhus Metopium* (Linn.), or perhaps the *Moronobea grandiflora* (Choisy), natives of South America. This gum is quite distinct from the Hogg or Kuteera gum of India (*cf. Tragacanth*). Plants containing gums similar to acacia (*v.* Gm. 15, 195). *Para* and other gums (Pharm. J. [iii.] 18, 623, 745, and 1009).

TRAGACANTH AND ALLIED GUMS.

Tragacanth. *Tragacantha*, B.P.; U.S.P. *Gomme adragante*, Fr.; *Traganth*, Ger. A gummy exudate consisting in part of altered cells obtained either spontaneously or by means of incisions from the stems of various species of *Astragalus*, some of which occur in South Western Europe, while others are found in Greece and Turkey. The largest number, however, are indigenous in the mountainous regions of Asia Minor, Syria, Armenia, Kurdistan, and Persia. The tragacanth of commerce is produced in the last-named countries. In July and August, the shrubs are stripped of their leaves and short longitudinal incisions or slits are made in the trunks. The gum flows out, and, drying spontaneously, is ready for gathering in three or four days. If the weather is fine during the drying process, the 'white leaf' form of gum is obtained which is the most prized variety. If, however, rain falls or the wind rises, particles of dust collect on the surface of the gum which thereby loses its whiteness and becomes the 'yellow leaf' form, the second quality. The form of the pieces is determined by the shape of the incision; longitudinal incisions produce 'leaf' or flake tragacanth, punctures yield 'thread' tragacanth, while irregular shaped incisions give knob-like masses, generally coloured, and of relatively low value. Another form, known in Persia as 'Arrehbor,' exudes from branches which have been cut by a saw (Imp. Inst. Reports, 1909, No. 63).

When tragacanth is treated with water, one part dissolves and the other swells up, absorbing water, to the extent of even fifty times the weight of the gum used, the whole forming a thick mucilage. This may be diffused through more water when, on filtering, a soluble gum passes through, and there remains on the filter a slimy non-adhesive mucilage, *bassorin*, *tragacanthin*, or *adraganthin*. In presence of alkalis, the whole of the gum dissolves readily in water (Flück. a. Hanb. 178; Sandersleben, Phytochem. Untersuch. Leipzig, 1880, 90; Fremy, J. 1860, 504). On hydrolysis of three samples of white tragacanth, Widtsoe and Tollens (Ber. 33, 132) obtained fucose and arabinose, whilst fucose and xylose were obtained from two samples of brown tragacanth. Five different samples of tragacanth examined by Helger and Dreyfus (Ber. 33, 1178) were found to contain 9·4 to 15·4 p.c. of water; 3·1 to 2·7 of ash, also 15·1 to 22·4 p.c. of galactose (estimated as mucic acid) and 30 to 42 p.c. of arabinose (estimated as furfuraldehyde phenylhydrazone). A specimen of vermicelli tragacanth contained 4 p.c. of cellulose and 3 p.c. of starch. The samples obtained by artificial incision contain the larger proportions of water and ash.

Tragacanth gum, investigated by O'Sullivan, was found, like Gedda gum, to be a mixture of several gum acids. It can be separated into a group of acids which remain in solution in dilute alcohol, and an insoluble portion, for which the name *bassorin* is appropriated; *cf.* also von Fellenberg (Chem. Zentr. 1914, ii. 943) who finds that bassorin alone contains methoxyl (=5·38 p.c. MeOH); the soluble portion is methoxyl free. The acids of the soluble group were found to be built up on a nucleus acid, very similar if not identical with geddic acid, by its union with galactose and arabinose residues. The constitution of the insoluble portion has not been completely worked out; but it yields a nucleus acid of the formula $C_{14}H_{20}O_{13}$, to which the name *bassoric acid* is given, and also intermediate acids formed of bassoric acid united to the residues of xylose, and of a new pentose sugar, *tragacanthose*.

Allied gums. *Bassora*, *Kuteera*, or *Caramania gum*, *Hogg gum tragacanth*, consists of yellow or brown waxy masses. It comes from Persia, where it is said to be derived from almond and plum trees, and is employed in Smyrna in the adulteration of tragacanth (Flück. a. Hanb.). The *Cochlospermum Gossypium* (D.C.), a small deciduous tree growing abundantly in India, furnishes a gum which occurs in irregular rounded translucent lumps of a pale buff colour. The gum is sold in the Indian bazaars as a substitute for tragacanth, which it closely resembles. This gum has the property of slowly giving off acetic acid when exposed to moist air, a property also possessed by the gum of *Sterculia urens* (Roxb.) (Gurbourt, Pharm. J. 15, 57). This may be utilised for the detection of adulterants in gum Tragacanth. The material is treated with dilute phosphoric acid and steam distilled. Indian gum then gives about 7 times as much acetic acid as pure gum Tragacanth (Ann. Report Bureau of Chemistry, U.S. Dept. of Agriculture, Pharm. J. 1912, 34, 353; Emery, J. Ind. Eng. Chem. 4, 374; Fuller, Amer. J. Pharm. 1912, 84, 155). For the detection of acacia *see* gum arabic, above, and Frey (Apoth. Zeit. 1913, 28, 787). A stable acid, *gondic acid*, $C_{23}H_{30}O_{21}$, has been obtained from the gum of *Cochlospermum Gossypium* (D.C.) in the same manner as the arabic and geddic acids of O'Sullivan. On hydrolysis, the gum yields 18 p.c. of acetic acid, calculated on the dry and ash-free substance, and is thus an acetyl derivative. Xylose and a hexose are among the other products (Robinson, Chem. Soc. Trans. 89, 1496). *Cashew gum* is the exudation of the *Anacardium occidentale* (Linn.), a small tree indigenous to tropical America. *Cherry tree gum* behaves towards water in a similar manner to tragacanth. The insoluble portion consists of *cerasin*, combined with metals of the alkalis or alkaline earths (Fremy, J. 1860, 504). For hydrolysis of cherry tree gum, *v.* Hauers and Tollens (Ber. 36, 3306). *Linseed*, *marshmallow*, and *fleaseed gums* closely resemble tragacanth (Schmidt, Annalen, 51, 50; Frank, J. pr. Chem. [ii.] 95, 494; Kirchner and Tollens, Annalen, 175, 215; Hilger, Ber. 36, 3197). *Persian gum* (*v.* Pharm. J. [3] 20, 793) is of a hard glassy type, and its solutions in water are intermediate in character between those of tragacanth and gum arabic. The trade in this gum is considerable, but the commercial value is lower than that of either tragacanth or fine gum arabic (Imp. Inst. Report). *Wood gum* has been extracted from various woods, straw, loofah, and similar materials. It resembles cherry tree gum. On hydrolysis it yields xylose, and in some cases arabinose (Th. Thomsen, J. pr. Chem. [ii.] 19, 146; Poumarède and Figuer, Annalen, 64, 338; J. Soc. Chem. Ind. 1890, 335; Wheeler and Tollens, Ber. 22, 1046; 23, 137; Annalen, 254, 320; Allen and Tollens, *ibid.* 260, 289; Bader, Chem. Zeit. 19, 55; Johnson, Amer. Chem. J. 18, 24; Browne and Tollens, Ber. 35, 1457; Salkowski, Zeitsch. physiol. Chem. 34, 162).

Other Gums.

Agar agar. *Agar*, U.S.P. (admitted 1916; it is not in the British Pharmacopœia), *Bengal* or *Japanese isinglass*, is the dried jelly of *Gracilaria* (*Sphaerococcus*) *lichenoides*, Grev., *Gelidium corneum*, Lam., *G. cartilagineum*, Gaill., and other Red Algæ (*Rhodophyceae*) from China, Japan, Formosa, &c. (*see* Takao, J. Pharm. Chim. 1917, 15, 175). It consists mainly of a carbohydrate, *d-galactan* $(C_6H_{10}O_5)_x$, less correctly termed *gelose*, which is hydrolysed by acids to galactose, and is insoluble in cold water, alcohol, dilute acids, and alkalis. Agar yields on hydrolysis also small amounts of arabinose and fructose; on oxidation mucic acid is formed (Takao, *l.c.*). 1 part in 500 of boiling water forms a jelly on cooling (Morin, J. 1880, 1010; Porumbara, J. 1880, 1011; Bauer, J. pr. Chem. [ii.] 30, 375) (*v.* AGAR AGAR). 0·1 gram dissolved in 100 c.c. boiling water should give no precipitate on adding tannic acid (absence of gelatine) and should not be coloured blue by iodine (absence of starch). According to Takao (*l.c.*) the mucilage of some species, however, is coloured blue. 1 gram boiled with 100 c.c. of water for ten minutes, should set on cooling to a stiff jelly (U.S.P.). The material generally contains characteristic diatom skeletons, best recognised microscopically after ignition. Those of *Arachnoidiscus Ehrenbergii* are figured in Allen's Comm. Org. Analysis, 1911, vol. iv. p. 438. Agar (the Malayan plural is formed by repeating the singular) is used for preparing culture media in bacteriology, for making emulsions, for thickening ice-creams, and medicinally in chronic constipation. Its action in the latter case is purely mechanical; it passes through the intestine almost unchanged. (Trade names, Regulin, Agarase.) *Galactin*, a very similar gum to gelose, is found in the seeds of the *Leguminosæ* (Muntz, Bull. Soc. chim. 37, 409).

Amyloid gums. These are distinguished from most gums by being coloured blue by iodine. The more important are: *Amyloid* (distinct from that derived from cellulose), the soluble gum of the cotyledons of the tamarind and other plants; *Quince gum*, which breaks up into cellulose, gum, and sugar when heated with dilute sulphuric acid; and *Salep gum*, derived from the bulbs of orchids (Frank, J. pr. Chem. [ii.] 95, 479; Hilger, Ber. 36, 3197).

Animal gum. A gummy substance having the composition $C_{12}H_{20}O_{10},2H_2O$ has been isolated from the secretions of the salivary glands, from the brain, pancreas, kidneys, and other parts of the body. It is unaffected by the digestive ferments, but is converted into sugar by dilute acids. It reduces ammoniacal silver nitrate solution with formation of a mirror. With water, it gelatinises, forming a mucilage. It is insoluble in alcohol and ether (Landwehr, Zeitsch. physiol. Chem. 8, 122; 9, 367; 13, 122; Zeitsch. anal. Chem. 23, 601; 24, 640; Pouchet, Compt. rend. 20, 21; Folin, Zeitsch. physiol. Chem. 23, 347).

Fermentation gum. This gum, *Dextran* or *Viscose*, which occurs in the unripe sugar beet (Scheibler, Wag. J. 1875, 790), is formed in the lactic fermentation of cane sugar by the action of the bacterium *Streptococcus* (*Leuconostoc*) *mesenteroides* (van Tieghem, Jahresb. Agrik. Chem. 1879, 544; Béchamp, J. Th. 1881, 85; Bruning, Annalen, 104, 197). Formed also in mucic fermentation (Nageli, J. pr. Chem. [ii.] 17, 409). Dextran $C_6H_{10}O_5$ is amorphous, soluble in water and precipitated therefrom as an elastic thread-like mass by alcohol. By treatment with dilute sulphuric acid, sugar is obtained, and when oxidised with nitric acid, oxalic but no mucic acid.

Dextrin *v.* DEXTRIN.

Iceland moss gum. Two gums have been isolated from the jelly of Iceland moss, *Cetraria islandica* (Acharius). According to Hesse (J. prakt. Chem. 1916, [ii.] 93, 254) this lichen contains in the air-dry condition 80 p.c. of carbohydrate and 13–14 p.c. of water, and may be used for human food and fodder. The bitter taste is removed by 1 p.c. potassium carbonate. On hydrolysis with 6–8 p.c. sulphuric acid Iceland moss yields three times as much sugar (chiefly dextrose) as potatoes. Of the gums, *lichenin* $C_6H_{10}O_5$ is unaffected by iodine, while the other, *isolichenin*, is coloured blue by that reagent. Lichenin is a transparent brittle mass which dissolves in hot water, the solution gelatinising on cooling. It is soluble in solution of ammonio-copper sulphate; combines with bases; is converted by dilute acids into sugar; oxidised by nitric acid, it yields oxalic acid, and it reacts with glacial acetic acid, forming *triacetyl lichenin* $C_6H_7Ac_3O_5$ (Knop and Schnedermann, Annalen, 55, 165; J. 1847–8, 831; Errera, Inaug. Dis. Brussels, 1882, 18; Mulder, Annalen, 28, 279; Helger and Buchner, Ber. 23, 461). *iso*Lichenin is soluble in water, and unlike lichenin forms no acetyl derivative, nor is it soluble in ammonio-copper sulphate solution (Berg. J. 1873, 848; Errera; Hönig, Monatsh. 8, 452).

The lichen, *Evernia Prunastri* (Ach), contains a gum resembling lichenin, *evernin* ($C_6H_{14}O_7$ (Stüde, Annalen, 131, 241).

Irish-moss gum. Irish moss or carrageen, *Chondrus crispus* (Linn.), contains a gum which is soluble in water, insoluble in ammonio-copper sulphate, is not coloured blue by iodine and yields mucic acid when oxidised with nitric acid (Blondeau, J. 1865, 659; Flückiger and Obermeyer, J. 1868, 805; Painter, Pharm. J. [iii.] 18, 362). This seaweed is included in the U.S.P. (*Chondrus*). 1 part, boiled with 30 parts of water and strained, sets to a thick jelly on cooling. The dried plant contains about 64 p.c. of carbohydrate and 7 p.c. of protein. Hot water extracts the calcium salt of a colloidal ethereal sulphate; the calcium is freely ionised, but sulphate ions cannot be demonstrated until after hydrolysis (Haas, Bio-chem. J. 1921, 15, 469).

Sterculia gum, derived from various species of *Sterculia* (*v.* Maiden, Pharm. J. [iii.] 20, 381), *v. gums allied to tragacanth, supra.*

Sugar beet gum. Several forms of gum have been separated from the juice of the sugar beet. *Arabic* or *meta-arabic acid* (*cf. gum acacia*), *dextran* (*cf. fermentation gum*, *pararabin* (Reichardt, Ber. 8, 808), and *laevulan* (*v.* Lippmann, *ibid.* 14, 1509). Pararabin is a powder which forms a jelly with water of quite a different appearance from that obtained with meta-arabin. It is soluble in dilute acid solutions from which alkalis or alcohol precipitate it. Lævulan is a by-product in the extraction of crystallisable sugar from beet sugar molasses. When anhydrous, it is insoluble in water, but in its hydrated form it dissolves readily. When oxidised by nitric acid it yields mucic acid, and heated with dilute sulphuric acid it is entirely converted into lævulose.

Wine gum (*v.* Béchamp, J. 1875, 987; Chancel, J. 1875, 987; Neubauer, Zeitsch. anal. Chem. 15, 194).

Yeast gum (*v.* Hessenland, Zeit. Ver. Rübenzuck-Ind, 1892, 671; Salkowski, Ber. 1894, 27, 497, 925, 3325; Zeitsch. physiol. Chem. 1910, 69, 466; *ibid.* 1911, 73, 314; von Euler and Fodor, *ibid.* 1911, 72, 339; Meigen and Spreng, *ibid.* 1908, 55, 48; Harden and Young, Chem. Soc. Trans. 1912, 101, 1928). The preparation is more particularly described by Harden and Young; purification is best done as copper precipitate (Salkowski). Adherent glycogen is precipitated by saturation with ammonium sulphate; the filtrate is dialysed and the gum is then precipitated by alcohol. $[\alpha]_D$ is given from +66·76° to +91·1° by various authors; the higher figure is probably the most correct. On hydrolysis mannose and dextrose are formed, rather more of the former than of the latter. G. B.

GUM ACACIA *v.* Gums.

GUM AMMONIACUM *v.* Gum resins.

GUM ARABIC *v.* Gums.

GUM ASAFŒTIDA *v.* Gum resins.

GUM BENJAMIN *v.* Balsams.

GUM BENZOIN *v.* Balsams.

GUM, BRITISH, *v.* Dextrin.

GUM ELASTIC *v.* Rubber.

GUM GALBANUM *v.* Gum resins.

GUM GAMBOGE *v.* Gum resins.

GUM KINO *v.* Kino.

GUM LAC or **LAC RESIN** *v.* Resins.

GUM MYRRH *v.* Gum resins.

GUM THUS *v.* Resins.

GUMMIC ACID *v.* Gums.

GUMMI GUTTI *v.* Gamboge, art. Gum resins.

GUMMITE. An amorphous hydrated uranium oxide (UO_3, 61–75 p.c.) with some lead, calcium, silica, &c. It occurs as an alteration product of uraninite (pitchblende), and forms yellow to reddish brown gum-like masses, sometimes enclosing a nucleus of the unaltered parent mineral, and at times showing the external form of the original crystal. It is found together with other secondary uranium minerals at Johanngeorgenstadt, Schneeberg, and Annaberg, in Saxony, in the Elias mine (eliasite) at Joachimsthal in Bohemia, and rather abundantly in the Flat Rock and Deake mines in Mitchell Co., North Carolina.

Thorogummite ($UO_3 \cdot 3ThO_2 \cdot 3SiO_2 \cdot 6H_2O$) from Llano Co., Texas, pilbarite

$$(UO_3 \cdot ThO_2 \cdot PbO \cdot 2SiO_2 \cdot 4H_2O)$$

from Western Australia, and yttrogummite, an alteration product of cleveite from Norway, are related minerals. L. J. S.

GUN COTTON *v.* Explosives.

GUN METAL *v.* Tin.

GUNPOWDER *v.* Explosives.

GURHOFITE *v.* Dolomite.

GURJUN BALSAM. *Wood-oil*, *v.* Oleo-resins.

GURJUNIC ACID *v.* Oleo-resins.

GUROLITE or **GYROLITE** *v.* Calcium.

GUTTA PERCHA is the product obtained by coagulating the latex of certain species of *Palaquium* and *Payena*, belonging to the natural order *Sapotaceæ*, which are natives of the Malay Peninsula and Archipelago. The name is derived from two Malay words: *getah* and *percha* or *pertja*. The word *getah* is applied to any exudation from a tree, whilst *percha* or *pertja* refers either to the local name of the tree which was erroneously thought at first to furnish the product, or to the Malay name for Sumatra 'Pulau Percha.'

The introduction of gutta percha into commerce dates from 1843, when specimens were forwarded to London independently by two doctors resident in Singapore, Dr. William Montgomerie and Dr. José D'Almeida, and the remarkable properties of the material at once attracted attention. In 1847 the principal tree yielding gutta percha was described and named by Sir W. J. Hooker, and in the same year Dr. Ernst Werner von Siemens employed the material for insulating underground telegraph wires.

The principal trees yielding gutta percha of the best quality are *Palaquium Gutta*, Burck, *P. oblongifolium*, Burck, and *P. borneënse*, Burck. *P. oblongifolium* is considered by some botanists to be only a variety of *P. Gutta*; the common name for both in the Malay peninsula is Taban. A number of other species of *Palaquium* furnish gutta percha of second quality, the chief of these being *P. obovatum*, King (Taban putih), *P. Maingayi*, King and Gamble (Taban simpor), and *P.*

oxleyanum, Pierre (*Dichopsis pustulata*, Hemsley), which is variously known as Taban sutra, Taban putih, and Taban chaier in different parts of the Malay peninsula. *Payena Leerii* (Hook. and Benth.); and *P. Havilandi* (King & Gamble), furnish the white gutta percha known as Getah sundek or soondie.

There has been considerable confusion regarding the botanical identity of the trees yielding gutta percha, which has been increased by the fact that the same native name is frequently applied to distinct species in different districts.

Palaquium Gutta is a large forest tree which usually attains a height of about 60 feet and has a straight cylindrical trunk. Trees up to 150 feet or more in height and 4 to 5 feet in diameter have been recorded. The tree is easily recognised by its leaves, which are a beautiful coppery gold colour on the under surface and dark glossy green on the upper. They vary considerably in size, the leaves of mature trees being about 2 inches long, whereas those of young trees are much longer.

The geographical distribution of the trees which furnish gutta percha is curiously restricted, as they only occur naturally in a small area comprising the southern portion of the Malay peninsula, Sumatra, Banca, Borneo, Celebes, the Susu Islands, and the Philippines. The trees are not indigenous in Java but have been introduced and are now being cultivated there.

The latex is contained in isolated sacs which occur chiefly in the inner layers of the bark and also in the leaves. On making incisions in the bark the latex exudes and quickly coagulates, so that only a small yield of gutta percha can be obtained at one tapping. In consequence of this fact the Malays have adopted the destructive method of felling the trees in order to collect the gutta percha. The tree is cut down and incisions extending right round the trunk are made at intervals of 9 to 12 inches or even less. In the case of the best kinds of gutta percha, the latex exudes into the incisions where it quickly coagulates, and in about half an hour can be rolled off on a stick or scraped off with a knife. The latex of the inferior varieties does not coagulate so rapidly; it is collected in vessels placed underneath the incisions, and is afterwards coagulated by gentle heating. The gutta percha is subsequently boiled in water and made into blocks of various shapes.

The amount of gutta percha obtained per tree by the native method has been very variously stated, but it seems probable that the average return from 15 to 20 year old trees is not above 14 ozs. Large forest trees have, however, been known to yield over 2 lbs. of gutta percha, and a tree 160 feet high, in the Philippines, is stated to have furnished 8½ lbs.

In view of the serious destruction of the trees which is involved in the native method of obtaining the gutta percha, attempts are now being made in Perak and in Java to collect the product by tapping the standing trees. The average yield by this method is not yet definitely determined, but in Perak a tree 59½ inches in girth has yielded 1 lb. 3¾ ozs. of gutta percha in 21 tappings extending over 6 weeks. Gutta percha is also being extracted by mechanical processes from the leaves of the trees. The older methods, involving the use of solvents, which were first employed for this purpose, have been abandoned, as it was found that the chemical treatment adversely affected the durability of the gutta percha when exposed to air and light.

Gutta percha resembles rubber in consisting essentially of a hydrocarbon, having the formula $(C_{10}H_{16})_n$, associated with resinous substances. It differs widely, however, from rubber in its physical properties. At ordinary temperatures it is hard - very tenacious, and cannot be stretched like rubber. On immersion in hot water it becomes soft and plastic so that it can be readily moulded; on cooling, it retains the shape given to it when soft and becomes hard but not brittle. When heated in the air, gutta percha decomposes and then takes fire, burning with a luminous smoky flame and giving off a characteristic odour resembling that of burning rubber. When submitted to destructive distillation, it yields a mixture of liquid hydrocarbons, including isoprene, similar to those obtained by the distillation of caoutchouc.

Gutta percha is not affected by weak mineral acids, strong hydrochloric or acetic acids, or strong alkalis, but is readily attacked by strong nitric or sulphuric acid. It is partially soluble in ether, alcohol, acetone, and cold petroleum spirit, which dissolve the resin; and completely soluble in carbon disulphide, chloroform, carbon tetrachloride, and hot petroleum spirit.

The hydrocarbon present in gutta percha, known as *gutta*, is the essential constituent and exhibits in an enhanced degree the characteristic properties of the product. When dissolved in chloroform and treated with chlorine, bromine, or iodine, *gutta* forms addition products, with some evolution of the halogen acid; and by the action of nitrogen oxides, nitrosites resembling those obtained from caoutchouc are formed.

Gutta percha slowly absorbs oxygen when exposed to air and light, and in the process the *gutta* is converted into a brittle resin. Gutta percha is, however, not energetically attacked by ozone like caoutchouc. Harries has shown that if gutta is dissolved in chloroform and treated with ozone, an ozonide $C_{10}H_{16}O_6$ is formed which, when decomposed by steam, gives a mixture of lævulic aldehyde and acid and lævulic aldehyde peroxide like the corresponding ozonide prepared from caoutchouc, but in different proportions. Harries concludes that the hydrocarbons of rubber and gutta percha are identical, both being probably 1 : 5 dimethyl*cyclo*octadiene (Ber. 1905, 38, 3985).

The resinous bodies associated with the gutta are oxygenated substances. They were separated by Payen in 1852 into two portions: (1) a crystalline white resin, soluble in hot but insoluble in cold alcohol, which he named *albane*; and (2) an amorphous yellow resin, soluble in cold alcohol, which he named *fluavile*. It seems probable from recent investigations that these substances are mixtures and not single compounds. In 1892 Oesterle discovered in gutta percha a fourth constituent, which he named *guttane* and found to contain C 86·4 p.c. and H 12·0 p.c. For information on the composition and chemical properties of gutta percha *see* papers by Ramsay, Chick, and Collingridge, and by Caspari in J. Soc. Chem. Ind. 1902, 21, 1367; 1905, 24, 1274.

In the analysis of crude gutta percha, it is customary to determine the moisture, the resin, the gutta, and the insoluble matter (dirt). The moisture is usually determined by heating a weighed quantity in an air or water oven, or *in vacuô*, until no further loss in weight occurs; sometimes the water given off is collected and weighed. The resins are determined by extraction with hot acetone in a Soxhlet apparatus, or by ether or petroleum spirit in the cold; the solvent is distilled off and the resin weighed. The residue left after removal of the resin is treated with chloroform which dissolves the gutta leaving the insoluble matter; the latter is removed by filtration, washed with chloroform, dried, and weighed. The gutta may be weighed after distilling off the chloroform, or it may be precipitated from the chloroform solution by the addition of alcohol and then dried and weighed.

The composition of several representative specimens of gutta percha, derived from trees belonging to a single species, which have been examined at the Imperial Institute, and by Obach, is given in the following table :—

Variety of gutta percha	Botanical source	Gutta	Resin	Dirt	Moisture	Ash
Getah taban merah [1]	*Palaquium Gutta* . .	70·6	13·9	0·7	14·8	0·95
” ” ”	” ” . .	68·3	13·4	8·1	10·2	0·89
Getah taban putih .	Uncertain . . .	35·6	49·5	7·4	7·5	0·72
Getah taban chaier .	” . . .	52·0	43·4	3·4	1·2	1·61
Getah simpor . .	*Palaquium Maingayi* .	44·9	45·5	8·4	1·2	2·13
Getah taban sutra[2] .	*Palaquium oblongifolium*	84·3	10·7	3·7	1·3	—
Getah sundek[2] .	*Payena Leerii* . .	43·9	37·6	5·1	13·4	—

[1] Obtained by tapping standing trees.

[2] Analyses by Obach

The commercial brands of gutta percha vary very considerably in composition and quality. They are usually designated by the names of the countries in which they are produced or of the ports from which they are shipped. Obach has classified the 12 principal brands into four groups as follows :—

I. First quality—genuine from *P. Gutta* or *oblongifolium* and allied species: (1) Pahang from the Malay peninsula, (2) Bulongan red, and (3) Banjer red from Borneo;

II. Second quality—Soondie from *Payena* spp.: (4) Bagan goolie soondie, (5) Goolie red soondie, both from Borneo, and (6) Serapong goolie soondie from Sumatra;

III. Third quality—white, botanical source not definitely known: (7) Bulongan white, (8) Mixed white, (9) Banjer white, all from Borneo;

IV. Fourth quality—mixed and reboiled: (10) Sarawak mixed, (11) Padang reboiled, and (12) Banca reboiled.

Obach has given the average results of 571 analyses of these varieties, representing 2282 tons of raw gutta percha (*see* Cantor Lectures on Gutta Percha, published by the Society of Arts, Appendix v. 90–92). The figures for the genuine varieties may be given for comparison with those recorded above :—

—	Quantity represented by analyses		Percentage composition			
	Lots	Tons	Gutta	Resin	Dirt	Water
Pahang .	93	233	57·0	13·3	11·5	18·2
Bulongan red	37	60	51·8	18·2	10·8	19·2
Banjer red .	91	232	40·7	20·0	17·4	21·9

The treatment which crude gutta percha undergoes in the factory previous to its technical use may be briefly described. The lumps, after slicing if necessary, are softened by immersion in hot water and are then freed from impurities by treatment in a washing machine with hot water. The washed gutta percha while still soft is forced by pressure through wire gauze in order to remove any solid impurities which have not been eliminated in the washing process. The strained product is usually rewashed and is then transferred to the masticator or kneading machine, where the mechanically enclosed water and air are eliminated and the material rendered homogeneous. It is afterwards passed through a rolling mill and formed into sheets from $\frac{1}{8}$ to $\frac{1}{4}$ inch thick, which are cut into convenient lengths and stored in cellars until required for use. If it is desired to mix various kinds of gutta percha in order to obtain a product of a required composition, or to incorporate pigments, &c., the operation is conducted by means of a mixing machine fitted with specially shaped rollers which can be heated by steam.

In certain cases the crude gutta percha is washed with a hot 5 p.c. solution of sodium hydroxide in order to improve the colour. After treatment in this way, the product must be thoroughly washed with water to remove all trace of alkali.

The loss which results on cleaning raw gutta percha (*i.e.* the quantity of dirt and water present) is considerable, usually amounting to from 30 to 40 p.c. and sometimes to as much as 50 p.c.

For some purposes a very hard gutta percha is required, and this can be obtained by removing the resin from the ordinary material by extraction with solvents.

The physical and mechanical properties of gutta percha depend very largely on the proportions of gutta and resin present. Thus the temperature at which it softens; the time required to harden on cooling; the tensile strength; and the degree of elongation before breaking are all related to the value of the ratio gutta : resin.

The electrical properties, *i.e.* the insulation resistance, the inductive capacity and the dielectric strength, depend principally on the nature of the gutta and on the amount of water present, and are affected very little by the removal of the resin. (For determinations of the electrical properties of gutta percha, see Obach, *l.c.* 62-65.)

Gutta percha is employed for a variety of purposes, the chief of which are the insulation of submarine cables, and the manufacture of the covers of golf balls.

The amount of gutta percha which has been used in the cable industry forms a very large percentage of the total consumption. It was stated by Obach that of the 71,933 tons of raw gutta percha used in the United Kingdom from 1845 to 1896, at least two-thirds, and probably more, had been utilised for electrical purposes. The gutta percha employed for cable manufacture has to be specially selected for the purpose, as the insulating power of the different commercial brands varies enormously.

The gutta percha used for the covers of golf balls is hardened by removal of the resin in order to render it as tough and elastic as possible.

Gutta percha is also utilised for the manufacture of driving belts, rings, valves, &c., for pumps and hydraulic presses, boot soles, tubes, funnels, bottles, buckets, &c., for use with acid liquids, for cements (such as Chatterton's compound), for taking casts, and for surgical and many other minor purposes.

H. B.

GUVACINE, GUVACOLINE *v.* ARECA NUT.

GUYACAN. *Caesalpinia melanocarpa*, Griseb, a small tree of the family *Leguminosæ* growing in Argentina, yielding seed pods used locally as tanning agents. Guyacan resembles divi divi. Its tannin gives a blue black colour with iron-alum, and no precipitate with bromine water. It gives a pale yellow leather, plump, soft, and pliable.

GYNOCARDIC ACID. A term applied to the acids contained in the oil expressed from the seeds of *Gynocardia odorata*. Erroneously considered as identical with chaulmoogra oil (*cf.* Power and Gornall, Chem. Soc. Trans. 1904, 85, 838).

GYNOCARDIN *v.* GLUCOSIDES.

GYNOVAL *v.* SYNTHETIC DRUGS.

GYPSUM (Fr. *Gypse*; Ger. *Gyps*; Ital. *Gesso*). A common mineral composed of hydrated calcium sulphate $CaSO_4,2H_2O$, crystallising in the monoclinic system. The name *selenite* is sometimes applied to the clear crystallised variety, *satin-spar* to the finely fibrous variety, and *alabaster* (*q.v.*) to a compact, marble-like variety used for carving. The low degree of hardness (No. 2 on the scale) is a very characteristic feature: the mineral can be readily scratched with the finger-nail. Sp.gr. 2·32. The mineral is usually white, but sometimes greyish, yellowish, or reddish; and the glistening cleavage surfaces are usually conspicuous on a broken surface. The crystals possess a highly perfect cleavage in one direction parallel to the plane of symmetry; on the smooth, bright cleavage surfaces the lustre is pearly, and coloured bands (Newton's rings) are often to be seen. Cleavage flakes are flexible but not elastic (thus differing from mica), and when bent a fibrous cleavage is developed parallel to the faces of a pyramid: this fibrous cleavage is seen as silky striations on the principal cleavage, and is a very characteristic feature of gypsum.

Single crystals of gypsum, with a rhomb-shaped outline, are of common occurrence, embedded in clays. Fine groups of water-clear crystals are found in the sulphur mines of Sicily, the salt mines of Bex in Switzerland, and at many other localities. Enormous crystals, a yard in length, have been found in a cave in Wayne Co., Utah. Various types of twinned crystals are of common occurrence. The deposits of massive gypsum, such as are mined for economic purposes, occur as thick beds and nodular masses in sedimentary rocks of various geological periods. Those of the midlands of England are interbedded with the red marls and sandstones of Triassic age; those worked near Battle, in Sussex, belong to the later Purbeck beds: many of the deposits of the United States are of Palæozoic (Silurian, Devonian, and Carboniferous) age; whilst the important deposits in the Paris basin are of Tertiary (Eocene and Oligocene) age. These more extensive deposits of gypsum have been formed by the evaporation of water in inland lakes and seas, and they are often associated with beds of rock salt. The mineral has, however, in many cases originated by the action of water containing sulphuric acid and soluble sulphates (produced by the weathering of iron-pyrites and other sulphides) on limestone and other calcareous rocks. It is also formed by the action of volcanic vapours on the surrounding rocks.

The output of gypsum in England amounts to about a quarter of a million tons per annum; about half of this amount is mined in Nottinghamshire, considerable quantities in Staffordshire, Sussex, and Cumberland, and less in Derbyshire, Yorkshire, Westmoreland, and Somersetshire. The value ranges from 6 to 10 shillings per ton. In France, the output reaches 1½ million tons per annum, and about the same amount is produced in the United States. Nova Scotia and New Brunswick are also large producers. The French gypsum is remarkable in containing some admixed calcium carbonate and soluble silica, and for this reason it makes a harder plaster.

The principal use of gypsum is for the manufacture of plaster of Paris, stucco, and various kinds of wall-plasters and cements. Hence the popular name '*plaster-stone*.' The employment of plaster of Paris for making the moulds in the potteries has given rise to the name '*potter's stone*' for gypsum. In the tin-plate industry gypsum is used for polishing the plates; and it is added to water to give permanent hardness in brewing. The coarser grades of material are used as fertilizers (land plaster). Alabaster is used for carvings for inside decorations; and satin-spar is cut as beads and other small personal ornaments. Under the names 'terra alba,' 'annaline,' and 'satinite,' ground gypsum is used for adulterating paints and as a mineral loading in the manufacture of paper (*v.* CALCIUM).

References.—E. C. Eckel, Cements, Limes, and Plasters, 2nd ed. New York, 1907. R. W. Stones, Gypsum Products, their Preparation and Uses, U.S. Bureau of Mines, 1918, Technical Paper 155. D. C. Winterbottom, Gypsum and Plaster of Paris, Dept. of Chem. South Australia, 1917, Bull. No. 7. Special Reports on the Mineral Resources of Great Britain, Mem Geol. Survey, vol iii. 2nd ed 1918 G I Adams and others, Gypsum Deposits of the United States, Bull. U.S. Geol Survey, 1904, No 223. W. F. Jennison, Report on the Gypsum Deposits of the Maritime Provinces, Canada, Dept. Mines, 1911, Pub. No. 84 L. J. S

GYROPHORIC ACID $C_{16}H_{14}O_7$ is found in *Umbilicaria pustulata* (Hoffm.), *Gyrophora vellea* [(Linn.) Ach.], *Gyrophora spodochroa* [(Ehrh.) Ach.] and other lichens. It crystallises in needles from ether or dilute alcohol, melting at 202° with decomposition. Very easily soluble in acetone and alcohol. The alcoholic solution has an acid reaction, and gives a violet colour with ferric chloride. Is soluble in alkali to a yellow solution; boiling acetic acid converts it into orselline acid and boiling alcohol into orselline acid and its ethyl ester (Stenhouse, Annalen, 70, 218; Hesse, J. pr. Chem. [ii.] 58, 475; 62, 462, 63, 522; 68, 1; Zopf, Annalen, 300, 330, 313, 322, 317, 110; 338, 35; 340, 276; 346, 82).

H

"H" ACID. 1-Amino 8 naphthol-3 : 6-disulphonic acid.

HAARLEM BLUE. *Antwerp blue v.* PIGMENTS.

HÆMATEIN *v.* LOGWOOD.

HÆMATIN *v.* BLOOD.

HÆMATITE or **HEMATITE.** A mineral consisting of ferric oxide (Fe_2O_3), crystallising in the rhombohedral system, and an important ore of iron (*Fe, 70 p.c.*) According to whether *it is crystallised, massive, or earthy, it varies considerably in external appearance In all* cases, however, the mineral gives a characteristic *brownish red streak or powder*; and it is on account of this colour (resembling that of dried blood) that the mineral receives its name hæmatite, meaning, in *Greek, blood-stone. The* sp gr. of the crystals is 5·2, but of the compact and earthy varieties it may be as low as 4·2; hardness 6 (except in the soft, earthy varieties).

The crystals are iron-black with a brilliant metallic lustre, and they vary from rhombohedral to tabular in habit. This variety is distinguished as *iron-glance*, or *specular iron*; or, when the crystals are thin and scaly, as *micaceous iron-ore*. The compact varieties are distinguished as *red iron-ore* or *red hæmatite*. These sometimes exhibit a fibrous or columnar structure and a nodular surface, being then known as *kidney-iron-ore*; or, when the fibrous structure is so marked that the mineral breaks into rods, as *pencil-ore*. In these cases the material is often dark-red with a dull surface, but sometimes it may be iron-black with a sub-metallic to metallic lustre. Earthy, ochreous varieties are brighter red in colour, and are often mixed with clay and other impurities; these are known as *reddle, ruddle*, and *red iron-froth*.

Hæmatite occurs under a variety of conditions. The best crystals are found in connection with metamorphic silicate rocks and in mineral-veins; whilst the extensive masses of red iron-ore occur as bedded deposits in sedimentary rocks, often in association with limestone. The deposits on the east coast of the island of Elba, which have been extensively worked since the time of the Romans, consist of specular iron; whilst those of west Cumberland and north Lancashire, filling large irregular cavities in limestone, consist of red iron-ore and kidney-iron-ore.

Besides being used as an ore of iron, hæmatite, in its harder, compact varieties, is used, to a limited extent, as a gem stone, and it was the material employed for some of the ancient *Babylonian cylinder seals. The pencil-ore* of Cumberland is cut and polished for mounting on scarf pins, &c., and for the burnishing tools used by jewellers and bookbinders. Ochreous varieties are used as a polishing material, and for making red paint and red pencils.

L. J. S.

HÆMATOGEN, HÆMOL. Trade names for albuminates *of iron used in the treatment* of anæmia.

HÆMATOXYLIN *v.* LOGWOOD.

HÆMOGLOBIN *v.* BLOOD.

HAIDINGERITE *v.* CALCIUM

HALFA. *Alfa, alea.* Arabic name for *Stipa tenacissima* (Linn.); especially applied to the Esparto grass from Algeria.

HALITE or **ROCK-SALT** (Fr. *Sel gemme*; Ger. *Steinsalz*). Sodium chloride NaCl, crystallised in the cubic system. Although known as a mineral since remote times and of very wide distribution, the name halite (from ἅλς, salt) is comparatively recent (E. F. Glocker, 1847). Well-developed crystals with the form of simple cubes are not uncommon, but those of octahedral habit are quite rare. The faces of the cube sometimes show sunken depressions, though not so marked as in the hopper-shaped crystals produced artificially. Small square pits or etched figures are readily produced on the cube faces by solution. Silky, fibrous masses also occur. But most frequently the mineral is found as granular or sparry masses with bright cleavage surfaces. This perfect cleavage, parallel to the faces of the cube, is an important character. In addition, the crystals sometimes break along surfaces (glide-planes) parallel to the rhombic-dodecahedron. This effect is, however, secondary, and is only produced after the crystal has been subjected to pressure, either naturally by earth movements or by artificial means. If a cleavage cube of salt be placed diagonally in a vice so that two cube edges are held by the jaws, it can be broken in this direction. The plastic deformation of rock-salt and the percussion-figure (a four-rayed star with the rays parallel to the diagonals of the cube face, which is produced on a cleavage surface by a smart blow with a blunt point) also depend on the presence of these planes of gliding.

Crystals are usually colourless and transparent, but occasionally they are of a deep blue or violet colour. This colour disappears when the salt is dissolved in water or when heated; and it can be produced artificially by the vapour of alkali metals or by the action of cathode or radium rays. It has been variously ascribed to the presence of metallic sodium, subchloride Na_2Cl, sulphur, or as an optical effect produced by thin cavities. Sp. gr. of pure crystals, 2·17; H. 2½. Specific heat, 0·219. The mineral is a non-conductor of electricity and is highly diathermanous. It is therefore used as blocks and lenses for experiments on radiant heat. The best crystallised material is obtained from Stassfurt in Prussia, and from Wieliczka and Kalusz in Poland; good, clear cleavage blocks have been found at Meadowbank in Cheshire. Crystals are very nearly pure sodium chloride, and mixed crystals with potassium chloride (sylvite) do not occur. Massive material contains impurities of various kinds (v. SODIUM CHLORIDE). A variety known as *huantajayite*, containing AgCl 11 p.c., is found as small cubes at Huantajaya near Tarapaca in Chili.

Rock-salt is most frequently found as bedded deposits in sedimentary rocks, such as sandstone, shale, clay, and less often limestone, and is frequently associated with beds of gypsum and anhydrite, and sometimes with petroleum. Such deposits have evidently been formed in inland seas and lakes under desert conditions; they are of world-wide distribution and are met with in formations of all geological periods, as indicated below.

Geological formations	Localities
Recent	Dead Sea, Caspian Sea, Great Salt Lake of Utah, California, &c.
Pliocene	Volterra in Tuscany, Parajd in Transylvania.
Miocene	Wieliczka and Kalusz in Poland, Bukovina, Minglanilla in Spain.
Oligocene	Eastern Carpathians in Transylvania, Wittelsheim in Alsace.
Eocene	Cardona near Barcelona, Caucasus, Roumania.
Cretaceous	Unna in Westphalia, Medea in Algeria, Texas, Louisiana, Peru.
Jurassic	Bex in Switzerland, Rodenburg in Hesse Nassau, Peru.
Triassic—	
Keuper	Cheshire, Worcestershire, Lancashire, north-east Yorkshire, Durham, Isle of Man, Antrim, Pyrenees, Lorraine, Celle in Hanover, Berchtesgaden in Bavaria, Hall in Tyrol, Hallein in Salzburg, Ischl and Hallstatt in Upper Austria, Aussee in Styria.
Muschelkalk	Friedrichshall in Württemberg, Ernsthall in Thuringia.
Triassic: *contd.*	
Bunter	Schöningen in Brunswick, Arnshall in Thuringia.
Permian	Stassfurt, Halle, &c., in Prussian Saxony, Artern in Thuringia, Sperenberg near Berlin, Segeberg in Holstein, Inowrazlaw in Posen, Orenburg in Russia, Kansas.
Carboniferous	Pennsylvania, Virginia, West Virginia, Michigan, Ohio, New Brunswick, Nova Scotia.
Devonian	Westphalia, Baltic provinces of Russia, Siberia, China.
Silurian	New York, Michigan, Ohio, Ontario.
Cambrian	Salt Range in Punjab.

In addition to these bedded deposits of rock-salt, which are the only deposits of economic importance (v. SODIUM CHLORIDE), mention may be made here of some other modes of occurrence. The microscopic cavities present in vast numbers in the quartz of granitic igneous rocks often contain minute cubes of halite together with water and liquid carbon dioxide. The saline encrustations of active volcanoes (e.g. Vesuvius), produced either by direct sublimation or by the action of acid vapours on the scoria, contain sodium and potassium chlorides, usually in a powdery form, but occasionally as distinct crystals of halite and sylvite.

References.—For a detailed *résumé* of the mineralogical characters and occurrence of halite, v. C. Hintze, Handbuch der Mineralogie, Leipzig, 1911, vol. i. pp. 101–231; on the deposits worked commercially, v. J. O. von Buschman, Das Salz, dessen Vorkommen und Verwertung in samtlichen Staaten der Erde, 2 vols. Leipzig, 1906–9. A. F. Calvert, Salt in Cheshire, London, 1915. L. J. S.

HALLOYSITE. An uncrystallised clay-mineral with approximately the composition of kaolinite (*q.v.*) but containing rather more water (about 19 p.c.). It forms compact masses with a slight greasy feel and lustre, and may be white, grey, or shades of various colours; sp.gr. 2·0–2·2; H. 1–2. It occurs as beds in sedimentary rocks and as masses in mineral-veins, and has sometimes been observed as a decomposition product of granite and other rocks containing felspar. Possibly the minute amorphous granules of china-clay and some other clays may be referable to this species. (*See* H. Ries, Clays, their Occurrence, Properties, and Uses, 2nd ed. 1908.) L. J. S.

HÄLLEFLINTA v. HORNSTONE.

HALOGEN. A term originally applied by Berzelius to the group of non-oxygenated electro-negative radicles, simple and compound, which combine with metals to form salts known as *haloid salts*. Usually restricted to the four elements—Fluorine, Chlorine, Bromine, and Iodine.

HALOGEN ACETIC ACIDS. Derivatives of acetic acid in which the hydrogen of the methyl group is partly or wholly replaced by a halogen.

Chloroacetic Acids.

Monochloroacetic acid $CH_2Cl{\cdot}COOH$. Prepared by passing chlorine into acetic acid alone (Hoffmann, Annalen, 102, 1), or in the presence of iodine (Müller, *ibid.* 133, 156), sulphur (Auger and Béhal, Bull. Soc. chim. [iii.] 2, 145), or red phosphorus (Russanow, J. Russ. Phys. Chem. Soc. 23, 222); by the action of chlorine on acetyl chloride in the presence of iodine (Jazukowitsch, Zeitsch. Chem. 1868, 234); by the interaction of chlorine, glacial acetic acid, and acetic anhydride at 100° (Hentschel, Ber. 1884, 17, 1286); together with acetyl chloride by the action of chlorine on acetic anhydride at 100° (Gal, Annalen, 122, 374); by the interaction of ethylene and chlorine peroxide (Furst, *ibid* 206, 78); by heating trichloroethylene with sulphuric acid containing a small amount of water (Simon and Chavanne, U.S. Pat. 1304108; J. Soc. Chem. Ind. 1919, 35, 553A).

Crystallises in two modifications, *a*- prisms, m.p. 61·8°; *β*- plates, m.p. 56·01°. By evaporating an aqueous solution or by melting the solid substance, the *β*- modification is produced; this changes to the *a*- form on the addition of a crystal of the latter (Pickering, Chem. Soc. Trans. 1895, 665, 670; *cf.* Tollens, Ber. 1884, 17, 665; Tanatar, J. Russ. Phys. Chem. Soc. 24, 694); b.p. 185°–187°, 104°–105°/20 mm (Sudborough and Lloyd, Chem. Soc. Trans. 1899, 476); sp.gr. 1·3978 at 64·5°; hydrates (Colles, *ibid.* 1906, 1252); heat of solution (Pickering, *l.c.*; Luginin, Ann. Chim. Phys. [v.] 17, 251; Tanatar, *l.c.*); heat of combustion 171·0 Cals. (Berthelot, *ibid.* [vi.] 28, 567); electrical conductivity (Kortright, Amer. Chem. J. 18, 368); magnetic rotation (Perkin, Chem. Soc. Trans. 1896, 1236); esterification constant (Sudborough and Lloyd, *l.c.*; *cf.* Lichty, Amer. Chem. J. 1895, 17, 27; 1896, 18, 590). Readily soluble in cold water, but on heating the solution decomposes into hydrochloric and glycollic acids (Buchanan, Ber. 1871, 4, 340, 863; Thomson, Annalen, 200, 75; Bevan, Proc. Camb. Phil. Soc. 1906, 13, 269; Senter, Chem. Soc. Trans. 1907, 460). Metallic hydroxides of the type $R'OH$ decompose it, yielding glycollic acid, whilst those of the type $R''(OH)_2$ yield diglycollic acid (Schreiber, J. pr. Chem. [ii.] 13, 346). By heating salts of chloroacetic acid with water in a sealed tube glycollic acid is produced (Kastle, Amer. Chem. J. 1892, 14, 586; Kastle and Keiser, *ibid.* 1893, 15, 471; *cf.* Euler, Ber. 1906, 39, 2726). On distilling the acid *in vacuô* with phosphorus pentoxide, the anhydride

$$(CH_2ClCOO)_2O$$

is produced, whilst by distilling the acid through a heated tube, carbon monoxide, hydrogen chloride, *sym*-dichloromethyl ether and trioxymethylene are the products (Grassi-Cristaldi, Gazz. chim. ital. 27, ii. 502). On heating with 4 parts of phosphorus pentachloride, it yields carbon tetrachloride and other products (Michael, J. pr. Chem. [ii.] 35, 96); with ammonia glycine is produced. By interaction with sodium sulphide and sulphur in alkaline solution a dithioglycollic acid is produced, which on reduction, yields thioglycollic acid (Kalle & Co. D. R. P. 180875; Chem. Soc. Abstr. 1907, i. 1008). By the electrolysis of the potassium salt acetic acid, carbon dioxide and chlorine are formed, hydrogen not being evolved until the potassium salt is completely decomposed (Lassar Cohn, Annalen, 251, 335; *cf.* Bunge, J. Russ. Phys. Chem. Soc. 24, 690). By heating the dry silver salt, silver chloride and glycollide are produced (Beckurts and Otto, Ber. 1884, 14, 576). The sodium salt or the ethyl ester react with potassium cyanide to yield the corresponding derivatives of cyanacetic acid (Phelps and Tillotson, Amer. J. Sci. 1908, [iv.] 26, 267, 275). For interaction with tertiary amines to yield betaines, *v.* Reitzenstein, Annalen, 1903, 326, 305; with aniline, *v.* Vallée, Bull. Soc. chim. 1905, [iii.] 33, 966; with hydroxylamine, *v.* Rivals, Compt. rend. 1896, 122, 1489; with thiocyanic acid or its salts, *v.* Nencki, J. pr. Chem. [ii.] 16, 1; Jager, *ibid.* 17; with phenols, *v.* Saarbach, *ibid.* 21, 151; with nitrogen sulphide, *v.* Francis, Chem. Soc. Trans. 1905, 1839.

Methyl ester. Prepared by passing chlorine into methyl acetate at 110°–120° (Censi, Bull. Soc. Ind. Mulhouse, 70, 311), and as ethyl ester (*q.v.*); b.p. 115° (Censi, *l.c.*), 130° at 740 mm. (Schreiner, Annalen, 197, 8; *cf.* P. Meyer, Ber. 1875, 8, 1152); sp.gr. 1·2352 at 19·2° (Henry, J. 1885, 1329).

Ethyl ester. Prepared by the interaction of chloracetyl chloride and alcohol (Willm, Annalen, 102, 109), or by the action of alcohol on monochloroacetic acid in the presence of sulphuric acid (Conrad, *ibid.* 188, 218); b.p. 144·5°–144·9° at 754·2 mm.; sp.gr. 1·1585 at 20°/4° (Brühl, *ibid.* 203, 209). Condensation products are formed with ethyl sodiomalonate (Michael, Ber. 1905, 33, 3217); benzylamine (Mason and Winder, Chem. Soc. Trans. 1894, 628); phenylhydrazine (Reissert, Ber. 1895, 28, 1231; Busch, Schneider and Walter, *ibid.* 1903, 36, 3877; Meussdörffer, J. pr. Chem. 1907, [ii.] 75, 121); substituted ureas (Dixon, Chem. Soc. Trans. 1897, 628); magnesium ethyl bromide (Süsskind, Ber. 1906, 39, 225); magnesium phenylamine iodide (Bodroux, Compt. rend. 1905, 140, 1597).

Dichloroacetic acid $CHCl_2{\cdot}COOH$. Prepared by chlorinating acetic acid (Maumené, Annalen, 133, 154; Müller, *ibid.* 159); by the interaction of chloral and potassium cyanide (Wallach, Ber. 1873, 6, 114; Annalen, 173, 295; Kötz, Chem. Soc. Abstr. 1910, i. 151); by passing chlorine into phloroglucinol (Hlaziwetz, Annalen, 155, 132; Zincke and Kegel, Ber. 1889, 22, 1476); by the interaction of perchlorethylene and sodium ethoxide at 120° (Geuther and Fischer, J. 1864, 316); of hexachlorotriketohexylene and water (Zincke and Kegal, *l.c.*); of pyrrol and sodium hypochlorite (Ciamician and Silber, Ber. 1885 18, 1764); of trichloroacetic acid and sodium or barium hydroxides (Pinner, *ibid.* 757); by hydrolysing the ethyl ester (*q.v.*).

Colourless liquid, m.p. −10·8° (Pickering, Chem. Soc. Trans. 1895, 667); b.p. 189°–191°; sp.gr. 1·5724 at 13·5°; mag.rot. (Perkin, *ibid.* 1896, 1236); esterification constant (Sudborough and Lloyd, Chem. Soc. Trans. 1899, 476). Slowly decomposed by heating with water in a sealed tube at 100°, more rapidly with sodium or barium hydroxides (*cf.* Timoféeff, J. Russ. Phys. Chem. Soc. 1904, 36, 255). By heating with silver oxide and a small quantity of water silver chloride and glyoxylic acid are produced (Beckurts and Otto, Ber. 1881, 14, 583). On electrolysis of an aqueous solution hydrogen, carbon monoxide, carbon dioxide, and an oil containing chlorine are produced (Troeger and Ewers, J. pr. Chem. [ii.] 58, 125). The potassium salt yields potassium chloride, trichloroacetic acid, and other products on dry distillation (Friedrich, Annalen, 206, 244). Dichloroacetic acid reacts with phosphorus pentachloride (Michael, Amer. Chem. J. 9, 215); aniline and its homologues (Cech and Schwebel, Ber. 1877, 10, 179; Heller, Annalen, 1904, 332, 247; 1908, 358, 349; Ber. 1908, 41, 4264; Ostromisslensky, *ibid.* 1907, 40, 4972; 1908, 41, 3019; Heller and Aschkenasi, Annalen, 1910, 375, 261), thiourea (Dixon, Chem. Soc. Trans. 1893, 816); nitrogen sulphide (Francis, *ibid.* 1905, 1838).

Methyl ester, b.p. 142–144° (Wallach, Annalen, 173, 299), sp.gr. 1·3808 at 19·2 (Henry, *l.c.*).

Ethyl ester. Prepared by chlorinating alcohol (Altschul and Meyer, Ber. 1893, 26, 5757); by the interaction of chloral, alcohol, and potassium cyanide (Wallach, *ibid.* 1876, 9, 1212; 1877, 10, 1526); or of dichlorinated vinyl ethers and alcohol (D. R. PP. 209268, 210502, 212592; Chem. Soc. Abstr. 1909, i. 453, 694, 873); b.p. 157·7° at 751·6 mm. (Schiff, Annalen, 220, 108); sp.gr. 1·2821 at 20°/4° (Bruhl, *ibid.* 203, 22). With sodium or silver it yields maleic ester (Tanatar, Ber. 1879, 12, 1563).

Trichloroacetic acid $CCl_3{\cdot}COOH$. Prepared by chlorinating acetic acid in the sunlight (Dumas, Annalen, 32, 101); by the oxidation of chloral with fuming nitric acid (Kolbe, *ibid.* 54, 183; Clermont, Ann. Chim. Phys. [vi.] 6, 135; Judson, Ber. 1870, 3, 782; Thurnlackh, Annalen, 210, 63; Tommasi and Meldola, Chem. Soc. Trans. 1874, 314), chromic acid (Clermont, Compt. rend. 76, 774), or potassium permanganate (Clermont, *ibid.* 86, 1270).

M.p. 57° (Sudborough and Lloyd, Chem. Soc. Trans. 1899, 476); sp.gr. 1·6298 at 60·6°; heat of combustion (const. press.) 92·8 Cals. (Berthelot, Ann. Chim. Phys. [vi.] 28, 569); electrical conductivity (Rivals, Compt. rend. 125, 274; Ostwald, Zeitsch. physikal. Chem. 1, 100; 3, 177; Carrara, Gazz. chim. ital. 27, i. 207); esterification constant (Sudborough and Lloyd, *l.c.*; Kailan, Monatsh. 1908, 29, 799), mag.rot. (Perkin, Chem. Soc. Trans. 1896, 1236). At 300° it decomposes into triacetyl chloride, carbon dioxide, and hydrogen chloride (Engler and Steude, Ber. 1893, 26, 1443), whilst the silver salt yields the anhydride, silver chloride, carbon monoxide, and carbon dioxide (Beckurts and Otto, Ber. 1881, 14, 576); for sodium salt, *cf.* Henry, *ibid.* 1879, 12, 1844. At 200° with iodine trichloride perchloromethane, hydrogen chloride, and carbon dioxide are produced (Krafft, *ibid.* 1876, 9, 1049). Chloroform and carbon dioxide are produced by heating the acid with water or alkalis (Dumas, *l.c.*; Otto, Ber. 1871, 14, 589; Seubert, *ibid.* 1875, 18, 3342), potassium cyanide (Bourgoin, Compt. rend. 94, 448), aniline (Goldschmidt and Braüer, Ber. 1906, 39, 109), tertiary bases (Silberstein, *ibid.* 1881, 17, 2664), antipyrine (Stollé, Ber. Deut. pharm. Ges. 1910, 20, 371), or with resorcinol or cresol, but phenol or thymol yield hydrogen chloride, carbon monoxide, and phosgene (Anselmino, *ibid.* 16, 390). Reduction with potassium amalgam or hydriodic acid gives acetic acid. The sodium or zinc salt yields on electrolysis trichloromethyl trichloroacetate (Elbs and Kratz, J. pr. Chem. [ii.] 55, 502). For compounds with aldehydes and ketones, *v.* Koboseff, J. Russ. Phys. Chem. Soc. 1903, 35, 652; Plotnikoff, *ibid.* 1904, 36, 1088; 1905, 37, 875; Ber. 1906, 39, 1794).

Methyl ester. B.p. 152·3°–152·5° at 765·3 mm. (Schiff, Zeitsch. physikal. Chem. 1, 379; *cf.* Anschutz and Haslam, Annalen, 253, 124); sp.gr. 1·4892 at 19·2° (Henry, J. 1885, 1329).

Ethyl ester. Prepared by the interaction of trichloroacetic acid and alcohol with sulphuric acid (Clermont, Compt. rend. 1901, 133, 737), or with hydrogen chloride (Spiegel, Ber. 1907, 40, 1730); b.p. 164°; sp.gr. 1·369 at 15° (Claus, Annalen, 191, 58; Bruhl, *ibid.* 203, 22; Schiff, *ibid.* 220, 108). With ammonia it yields the amide; with sodium ethoxide, orthoformic ester, sodium ethyl carbonate, and sodium chloride are the products (Klein, Chem. Soc. Trans. 1877, i. 291).

Bromoacetic Acids

Monobromoacetic acid $CH_2Br{\cdot}COOH$. Prepared by the action of bromine on acetic acid, either alone (Perkin and Duppa, Annalen, 108, 106) or in the presence of carbon disulphide (Michael, Amer. Chem. J. 5, 202), or of sulphur (Genvresse, Bull. Soc. chim. [iii.] 7, 364); by the interaction of chloroacetic and hydrobromic acids at 150° (Demole, Ber. 1876, 561), by the oxidation of ethylene dibromide with fuming sulphuric acid (Kachler, Monatsh. 2, 559), or of monobromoacetylene in alcoholic solution by air (Glockner, Annalen, Suppl. 7, 115).

M.p. 49°–50°; b.p. 117–118°/15 mm. (Sudborough and Lloyd, Chem. Soc. Trans. 1899, 477), 196° (Lassar-Cohn, Annalen, 251, 342). On heating an aqueous solution of the acid it is slowly decomposed into glycollic acid (Senter, Chem. Soc. Trans. 1909, 1828). Electrical conductivity (Ostwald, Zeitsch. physikal. Chem. 3, 178; Kortright, Amer. Chem. J. 18, 368). By heating the acid with silver powder at 130°, succinic acid is formed, whilst with silver nitrate silver glycollate is produced (Senter, Chem. Soc. Trans. 1910, 346). Nitrogen sulphide yields bromoacetamide and bromodiacetamide (Francis, *ibid.* 1905, 1839). The sodium salt heated *in vacuo* yields glycollide. The potassium salt gives on electrolysis acetic acid, bromine, and carbon dioxide, no hydrogen being evolved until the potassium salt is completely decomposed (Lassar-Cohn, *l.c.*). Monobromoacetic acid has been used as a reagent for detecting albumin in urine (Boymond, J. Pharm. Chim. [v.] 20, 482).

Methyl ester. Prepared by heating methyl alcohol and monobromoacetic acid in sealed tubes at 100° (Perkin and Duppa, Annalen, 108, 109); b.p. 144°.

Ethyl ester. Prepared as methyl ester, or together with other products by the interaction of sodium ethoxide and bromine (Sell and Salzmann, Ber. 1874, 7, 496); b.p. 159°. It undergoes numerous condensations: with magnesium it yields ethyl acetoacetate and ethyl γ-bromoacetoacetate (Stollé, Ber. 1908, 41, 954); with ethyl oxalylacetate, ethyl citrate (Lawrence, Chem. Soc. Trans. 1897, 458); with ethyl sodioacetoacetate, ethyl acetosuccinate (Sprankling, *ibid.* 1165); with ethyl dimethylacetoacetate, ethyl $\alpha\alpha\beta$-trimethyl-β-hydroxyglutarate (Perkin and Thorpe, *ibid.* 1178).

For other esters, *v.* Clarke, *ibid.* 1910, 428; Steinlen, Bull. Acad. roy. Belg. [iii.] 34, 101; Kunckell and Scheven, Ber. 1898, 31, 172).

Dibromoacetic acid $CHBr_2{\cdot}COOH$. Prepared by the action of bromine on acetic acid alone (Perkin and Duppa, Annalen, 110, 115), or in the presence of sulphur (Genvresse, Bull. Soc. chim. [iii.] 7, 478); by the hydrolysis of the ethyl ester (*q.v.*); m.p. 48°; b.p. 232°–234°; esterification constant, *v.* Sudborough and Lloyd, Chem. Soc. Trans. 1899, 477. The silver salt, heated with water, yields silver bromide, glyoxylic acid, and dibromoacetic acid (Perkin, *ibid.* 1877, i. 91).

Ethyl ester. Prepared by the action of bromine on ethyl acetate at 160°; by passing bromine into alcohol (Schaffer, Ber. 1871, 4. 368); by the interaction of 4 parts of bromal hydrate with 1 part of alcoholic potassium cyanide (Remi, J. Russ. Phys. Chem. Soc. 7, 263); b.p. 192°.

Tribromoacetic acid $CBr_3{\cdot}COOH$. Prepared by the oxidation of bromal with fuming nitric acid (Schaffer, Ber. 1871, 4, 370; Gal. Compt. rend. 77, 786) or by heating an aqueous solution of malonic acid with bromine (Petriew, Ber. 1875, 8, 730). Monoclinic plates, m.p. 131° (Sudborough and Lloyd, Chem. Soc. Trans 1899, 477; *cf.* Gal, Annalen, 129, 56); electrical conductivity, *v.* Swartz, Chem. Zentr. 1898, ii. 703. On heating at 245° bromine and hydrogen bromide are evolved. By heating an aqueous solution of the acid or its salts, bromoform is produced. For compounds with aldehydes and ketones, *v.* Koboseff, J. Russ. Phys Chem. Soc. 1903, 35, 652; Plotnikoff, *ibid.* 1908, 40, 64, 1238).

Ethyl ester. Prepared by passing hydrogen chloride into a cooled alcoholic solution of tribromoacetic acid (Broche, J. pr. Chem. [ii.] 50, 98); b.p. 225°.

Chlorobromoacetic Acids

Chlorobromoacetic acid $CHClBr{\cdot}COOH$. Prepared by heating monochloroacetic acid (1 mol.) with bromine (1 mol.) in sealed tubes at 160° (Cech and Steiner, Ber. 1875, 8, 1174). Pungent smelling liquid, b.p. 201°; *ethyl ester,* b.p. 160°–163°; *amide,* m.p. 126°.

Monochlorodibromoacetic acid $CClBr_2{\cdot}COOH$. Prepared by heating monochlorodibromoacetaldehyde with fuming nitric acid (Neumeister, Ber. 1882, 15, 603); rhombic plates, m.p. 89°; b.p. 232°–234°, with decomposition. Potassium hydroxide converts it, on heating, into monochlorodibromomethane.

Dichloromonobromoacetic acid $CCl_2Br{\cdot}COOH$. Prepared by heating dichloromonobromoacetaldehyde with fuming nitric acid (Neumeister, *l.c.*); prisms, m.p. 64°; b.p. 215° with decomposition; readily soluble in water or alcohol. Potassium hydroxide converts it, on heating, into dichloromonobromomethane.

Iodoacetic Acids.

Mono-iodoacetic acid $CH_2I{\cdot}COOH$. Prepared by decomposing the ethyl ester (*q.v.*) with baryta water (Perkin and Duppa, Annalen, 112, 125); by heating acetic anhydride with iodine and iodic acid (Schützenberger, Zeitsch. Chem. 1868, 484). Prismatic needles, m.p. 82°; electrical conductivity (Walden, Zeitsch. physikal. Chem. 1892, 10, 647); esterification constant (Sudborough and Lloyd, Chem. Soc. Trans. 1899, 478).

Methyl ester. Prepared in the same manner as the ethyl ester (Aronstein and Kramps, Ber. 1881, 14, 604); b.p. 169°–171°.

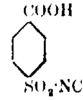
Ethyl ester. Prepared by the interaction of ethyl chloro- or bromoacetate, potassium iodide, and alcohol (Perkin and Duppa, *l.c.*); together with other products by heating di-iodoacetylene with excess of alcoholic potassium hydroxide (Nef, Annalen, 298, 348). Colourless oil with a penetrating smell; b.p. 69°/12 mm.; 75°–78°/16 mm. (Tiemann, Ber. 1898, 31, 825).

Di-iodoacetic acid $CHI_2{\cdot}COOH$. Prepared by the interaction of 1 part of malonic acid with 1 part of iodic acid in 4 parts of water; carbon dioxide is evolved, the solution is cooled, filtered, and allowed to stand. After 2 or 3 days crystals of tri-iodoacetic acid separate; these are filtered off and, after heating the filtrate, the di-iodo compound separates on cooling, m.p. 110° (Angeli, Ber 1893, 26, 596).

Ethyl ester. Prepared by the interaction of ethyl dibromoacetate and potassium iodide in alcoholic solution (Perkin and Duppa, Annalen, 117, 351), or of ethyl dichloroacetate and calcium iodide (Spindler, *ibid.* 231, 273). Yellow liquid, which cannot be distilled unchanged under atmospheric pressure.

Tri-iodoacetic acid $CI_3{\cdot}COOH$. For preparation, *v.* di-iodoacetic acid. Yellow plates, m.p. 150° with decomposition. By heating with acetic acid iodoform and carbon dioxide are produced.

HALAZONE. Trade name for *p*-sulphondichloramine benzoic acid



Used for the sterilisation of drinking water.

HALOTRICHITE. An iron-alum

$$FeSO_4{\cdot}Al_2(SO_4)_3,24H_2O$$

occurring naturally as silky, fibrous, efflorescent masses of a yellowish-white colour; named from ἅλς, salt, and θρίξ, τριχός, hair. It results by the action of the products of decomposition of iron-pyrites on surrounding aluminous rocks, as at Hurlet and Campsie near Glasgow; and also by the action of volcanic gases on rocks, as at the Solfatara di Pozzuoli near Naples, and in Iceland, where a variety called 'hversalt' is found. A large deposit occupies the crater of an extinct volcano near the source of the Gila river in Grant Co., New Mexico. At Urmia in Persia the mineral has been used for making ink.

L. J. S.

HAMAMELIN. A preparation from the witch-hazel *Hamamelis virginiana* (Linn.), either green or brown in colour, depending upon whether the leaves or bark have been used.

HAMAMELIS. The dried bark (*Hamamelidis Cortex*, B.P.) and leaves (*Hamamelidis Folia*, B.P.) of *Hamamelis virginiana* (Linn.), or witch-hazel, are used in pharmacy in tinctures, liquid extracts, solutions, and ointments.

HARDENED or **HYDROGENATED OILS.** The conversion of fluid oils into solid fats on a commercial scale is, perhaps, the most important development of recent years in the oil industry. Prior to the introduction of hydrogenation processes various methods of hardening oils had been tried. One of these was based on Varentrapp's reaction, according to which oleic acid is converted into palmitic acid by fusion with potassium hydroxide, but in practice the process was found to yield material of a bad colour, whilst the large amount of hydrogen liberated in the reaction was a source of danger.

Schmidt's process of heating oleic acid with zinc chloride at 185° requires a distillation of the product, and this is attended by partial decomposition of the β-hydroxystearic acid formed in the reaction, into oleic and iso-oleic acids. Better results were obtained by methods in which oleic acid was treated with sulphuric acid at a low temperature, and the resulting sulphonated compound decomposed by means of water into hydroxystearic acid and free sulphuric acid. By distillation of the hydroxystearic acid a mixture of oleic acid and its solid isomeride iso-oleic acid was obtained, the latter being of commercial value as a candle material. It is probable that this process has now been completely superseded by processes in which the oil is hydrogenated in presence of a catalytic agent.

In 1897 Tissier (Fr. Pat. 263158, 1897) claimed a process of converting oleic acid into stearic acid by means of the nascent hydrogen liberated when fats are heated with water and finely divided zinc in an autoclave, but Freundlich and Rosauer (Chem. Zeit. 1900, 566) found that the process did not produce the results claimed for it.

Electrolytic methods of hydrogenating oleic acid are claimed in the patents of Magnier, Brangier, and Tissier (Eng. Pat. 3363, 1900) and of Hemptinne (Eng. Pat. 1572, 1905). According to the latter, oleic acid is spread in a thin layer, on metallic plates, between which is passed an electric current, whilst the air in the vessel is replaced by hydrogen. Under these conditions hydrogen is absorbed, with the formation of a considerable proportion of stearic acid and other substances of higher m.p., and the process is repeated until about 20–30 p.c. of the oleic acid has been converted. The solid products are then separated by chilling and filtering the mixture.

Better yields were obtained in Böhringer's process (D. R. PP. 187788, 189332, 1906) in which the cathodes consisted of platinum coated with a layer of spongy platinum, or palladium coated with palladium black.

Development of Hydrogenation Processes. The modern methods of catalytic hydrogenation are based on the investigations of Sabatier and Senderens (Compt. rend. 1900, 130, 723; 131, 187), who showed that the unsaturated bonds in organic compounds could be made to absorb hydrogen, by treating the substances with the gas in the presence of a catalyst such as finely divided platinum.

A German patent for the hydrogenation of oils on these lines was taken out in 1902 by Le Prince and Siveke, whilst in 1903 Normann (Eng. Pat 1515, 1903) claimed a process of catalytically hydrogenating oils either in the form of vapour or as liquid. He stated, for example, that by suspending nickel powder in oleic acid heated in an oil bath, and passing a current of hydrogen or of a gaseous mixture rich in hydrogen, through the liquid, the oleic acid could be completely converted into stearic acid.

In Day's process (U.S. Pat. 826089, 1906) catalytic hydrogenation of hydrocarbon oils is employed to effect deodorisation, palladium black being preferably used as the catalyst.

An apparatus claimed by Schwoerer (D. R. P. 199909, 1906) consists of a vessel containing a helical trough the underside of which is coated with asbestos impregnated with nickel. The oily substance, *e.g.* oleic acid, is brought into a fine state of division by means of superheated steam, and passed, together with hydrogen, into the vessel, where the mixture is heated to 250°–270°. Under these conditions the hydrogen is absorbed, and the stearic acid deposited to a large extent in the trough. Bedford's process (Eng. Pat. 9112, 1908) is also concerned with the hydrogenation of oleic acid in vaporised form, the mixture of acid and hydrogen being made to pass through two separated layers of catalytic material in a vertical tower, the internal temperature of which is maintained at about 200°. The upper outlet of this tower delivers into a condenser connected with a receiver and a vacuum pump.

In his processes described in D. R. PP. 211669, 221890, 1907, Erdmann claims several modifications of a method of hydrogenating oils in the form of a fine spray in presence of a nickel or other catalyst. Thus the oil may be finely divided by means of a jet of hydrogen in a chamber containing a rotating cylinder covered with a layer of the catalytic agent, and is then made to pass through a bed of pumice impregnated with nickel. Or the oil may be introduced as a spray into a tower nearly filled with porous catalytic material, and there meet a current of hydrogen from another inlet, the temperature being maintained at 170°–180°. The solid product is preferably purified by distillation with steam under reduced pressure.

In the Kayser process, which is stated to be employed on a large scale in the United States, an inert powder such as kieselguhr is used as the carrier for a nickel catalyst, the oil being agitated with this at about 150°–160°. One form of apparatus used for effecting an intimate admixture of oil and catalyst consists of a horizontal cylinder in which revolves a paddle wheel the skeleton blades of which are covered with wire gauze. Hydrogen under pressure is introduced at one end of the cylinder, and the unabsorbed gas is drawn off at the other end.

Hydrogenation under pressure is also a feature of Testrup's process (Eng. Pat. 7726, 1910), the mixture of finely divided oil and catalyst being pumped into a vessel containing an atmosphere of hydrogen. For example, a mixture of oil and palladium may be heated to about 160° in a jacketed chamber provided with a stirring device, and then forced through nozzles into a second chamber, where the temperature is maintained at about 100°, and into which a current of hydrogen is passed under pressure. If still harder products are required, the process may be repeated in another chamber into which hydrogen is admitted at a still lower pressure, or a whole series of connected vessels may be used. (*See* Fig. 1.)

The use of autoclaves for hydrogenating oils has the advantage that the conversion is effected at a relatively lower temperature (100°–160°) thus obviating the risk of injury by over-heating. In Wilbuschewitz's process (Fr. Pat. 426343, 1910) an intimate mixture of the oil and catalyst is pumped or injected into a series of connected autoclaves, through which circulates a current of hydrogen in the opposite direction. The gas may be admitted in such a way that it disperses, in the form of a spray, the oily mixture accumulating in the bottom of the vessel, so that it can be pumped into connected autoclaves, where the process is repeated until the product has the desired m.p.; or the hydrogen may be introduced into the last autoclave, and the reduction continued in the succeeding autoclaves, with the aid of a reduction valve, and with a corresponding diminution in the pressure.

In the process claimed by Bedford and Williams (Eng. Pat. 29612, 1910) about 1 p.c. of a metal oxide catalyst is added to the oil, which is heated by means of a steam coil, in a closed vessel, to about 250°, while hydrogen is introduced through a perforated pipe at the bottom of the vessel. By using a mixture of hydrogen and oxygen in place of pure hydrogen, hydroxy fatty acids, or their compounds, may be produced by this process.

In order to effect the hydrogenation in stages at different temperatures Ellis has devised a method whereby the mixture of oil and metal catalyst is made to pass in a continuous stream through a long tube divided into a series of compartments, and encounters a current of hydrogen travelling in the opposite direction. A different temperature is maintained in the different compartments, *e.g.* 150° in the first, 165° in the second, and 180° in the last (Eng. Pat. 24084, 1912). In Pictet's process (Fr. Pat. 472080, 1913) the oil, with or without the addition of a catalyst, is made to pass by gravitation through a series of communicating tubes, the walls of which are composed of catalytic metal. Hydrogen is introduced in suitable proportion, and the oil is finely divided and brought into intimate contact with the gas by means of rotating devices which brush continually against the walls of the tubes.

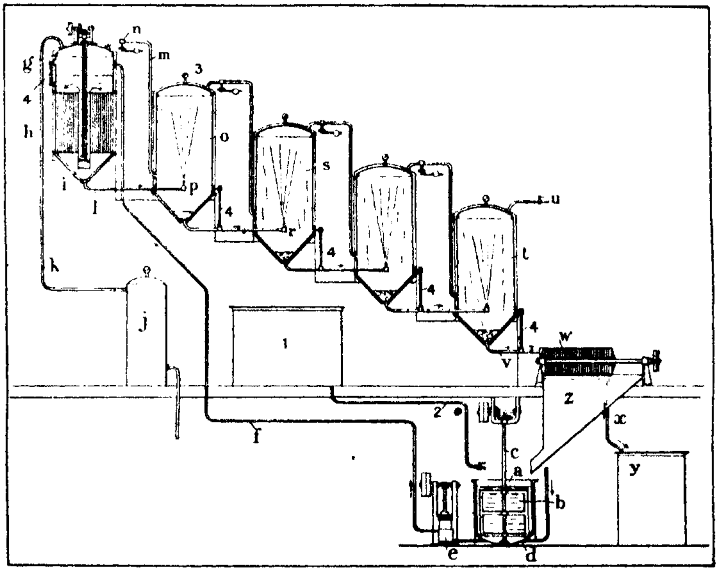


Fig. 1.

In order to obtain a large surface of catalytic material Dewar and Liebmann (Eng. Pat. 15668, 1914) distribute the catalyst over fibrous material such as yarn, which for strength may be enclosed between sheets of wire gauze. Or the fibrous material may be supported on frames attached to the agitator, or wound round the blades of the agitator in the hydrogenating apparatus.

In Calvert's hydrogenation process the oil is mixed with the catalyst and treated with hydrogen in a closed vessel containing a comb-shaped rotating agitator to subdivide the oil, whilst a centrifugal propellor at the base flings the mixture upwards to be beaten again.

The method of effecting minute subdivision of the oil adopted by Moore (U.S. Pat. 1121860, 1914) is to pass it together with the hydrogen through catalytic material which may be contained in a diaphragm porous to the oil and gas, but not to the catalyst.

Lane's apparatus (Eng. Pat. 968, 1915) consists of a vertical cylindrical vessel which is heated by means of a steam jacket or otherwise. Beaters rotating horizontally round a central shaft alternate with annular sloping shelves on the sides of the vessel, so that the oil and catalyst, entering at the top, are alternately sprayed outwards to the sides and guided to the centre of the beaters next below; and so on, until they reach the bottom and are then pumped again to the top. The hydrogen enters by a pipe at the base of the apparatus (Fig 2). In Walker's process (U.S. Pat. 1123962, 1915) the melted fatty acids or glycerides are sprayed by means of hydrogen under pressure against heated, finely divided, catalytic material, in presence of an electric discharge.

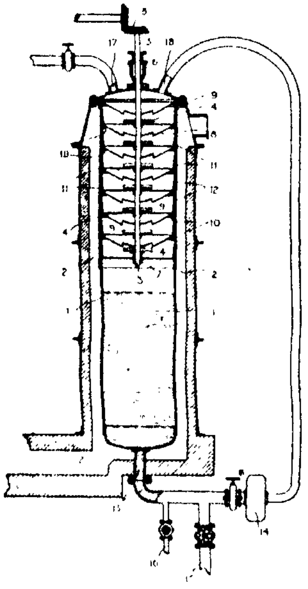


FIG 2

The essential features of the process of Birkeland and Devik (U.S. Pat. 1125259, 1915) are that the oil is mixed with the catalyst and a portion forced from a jet into an atmosphere of hydrogen, and thence downwards into the body of the oil, whereby hydrogen is conveyed by suction to the bottom of the vessel and is absorbed on rising through the oil.

McElroy (U.S. Pat. 1157993, 1915) claims the use of an emulsifying process. Freshly reduced nickel is mixed with the oil, and hydrogen is made to circulate through the liquid in minute ascending bubbles in a special form of apparatus, in such a way as to produce a gas-liquid emulsion.

In the process patented by Richardson U.S. Pat. 1177896, 1916) an electric arc is produced between nickel electrodes which are immersed in the oil, with the result that part of the metal is disintegrated and becomes incorporated with the oil. After hydrogenation the disintegrated metal is separated from the oil.

The apparatus devised by Maxted and Ridsdale (Eng. Pat. 109903, 1916) consists of a vertical column provided with baffle plates, so arranged that a mixture of oil, catalyst, and hydrogen, projected into the top of the vessel, is rotated alternately first in one direction and then in the other on its passage to the bottom.

A process for the simultaneous neutralisation and hydrogenation of oils is claimed by Schlinck and Co. (D. R. P. 334659, 1916), consisting in the addition of glycol and a catalyst before introducing hydrogen at a high temperature. The apparatus of the Soc. Anon. l'Oxyhydrique Française (Eng. Pat. 143848, 1920) contains tubular filtering devices of asbestos or biscuit porcelain, which serve for the introduction of the hydrogen in a fine state of division, and the separation of the catalyst from the oil.

The essential feature of the process of Wells (U.S. Pat. 1338887, 1921) is the vigorous agitation of the reaction mixture by the introduction of a stream of hydrogen from beneath.

Catalysts for Hydrogenation. In the original investigations on catalytic hydrogenation by Sabatier and Senderens finely divided platinum or palladium was used as the catalytic agent, but as nickel is a much less expensive catalyst than those metals it is now generally employed for the hydrogenation of oils and fats. Palladium is still used, however, in some works owing to its effecting the hydrogenation at a lower temperature (80–90°) and in a shorter time. According to Paal (Ber. 1908, 41, 2282) colloidal palladium effects very rapid hydrogenation of vegetable and animal oils and fats, whilst platinum black is much less effective than palladium for the purpose. The use of other metals such as cobalt, iron, and copper, as catalytic agents has also been claimed in several of the patent processes of hydrogenation.

In preparing a nickel catalyst the usual method is to precipitate nickel hydroxide from a solution of a salt such as nickel sulphate, in the presence of inert material such as kieselguhr, to dry the sludge and to reduce it in a current of hydrogen at a temperature of 300°–325°.

In Lane's process (Engineer, 1917, 511) solutions of nickel sulphate and of sodium carbonate are prepared in separate tanks provided with steam jets, and are transferred into a third tank provided with a mixing apparatus and containing indifferent material, such as kieselguhr. The mixture of precipitated nickel carbonate and kieselguhr is dried, ground up, and roasted to convert the carbonate into oxide, after which it is heated in a current of hydrogen.

One form of apparatus used for this purpose is a vertical vessel provided with external means of heating, and containing a series of reciprocating grids. The powdered material is introduced at the top and falls on to the successive grids, the movement of which exposes fresh particles to the current of hydrogen, which is admitted at the base, and rises through the grids to the outlet at the top of the apparatus. The reduced material falls into a vessel containing oil of the same kind as is to be hydrogenated.

and, after being thoroughly mixed, the oil mass is ground until of the desired consistency.

The method of preparing the catalyst has a considerable influence on its activity and its resistance to external influences. For example, nickel which has been reduced at as low a temperature as possible is more effective than that reduced at a higher temperature, but, on the other hand, is also more sensitive to the action of catalytic 'poisons.' Ellis (J. Soc Chem. Ind. 1912, 31, 1163) gives 300°–325° as a suitable temperature for the reduction. According to Kelber, however (Ber. 1916, 49, 1868), a catalyst prepared by reducing basic nickel carbonate with hydrogen at 450° is more sensitive to poisons than one prepared at 310°. A catalytic agent prepared by reducing a mixture of nickel salt with an inert inorganic medium at 450° proved remarkably resistant to the action of hydrocyanic acid, hydrogen sulphide, and carbon disulphide.

Reduced iron, sodium chloride, sodium sulphate, and sodium nitrate have no influence on the activity of nickel catalysts, but sodium sulphide gradually impairs the efficiency, and sulphur destroys it immediately (Moore, Richter, and Van Arsdel, J. Ind. Eng. Chem. 1917, 9, 451). Nickel may also be rendered inactive by traces of chlorine and of decomposition products in the oils undergoing hydrogenation. For this reason low-grade oils, such as whale and fish oils, may speedily render a nickel catalyst inactive. Heating and agitating the oil with freshly-precipitated copper hydroxide has been found an effective means of removing the poisonous constituents from such oils, especially after a preliminary treatment with sodium carbonate solution (Ellis and Wells, J. Ind. Eng. Chem. 1916, 8, 886). In some cases, however, it is necessary to hydrogenate the oil in two stages, filtering off the catalyst after it has become inactive. Veno (J. Chem. Ind., Tokyo, 1918, 21, 898) has shown that powdered metals (not reduced by hydrogen), such as nickel, tin, zirconium and copper, have but little injurious action on catalytic hydrogenation, but that iron, zinc, lead and mercury act as poisons,

The efficiency of a catalytic metal is considerably increased by distributing it over a porous non-catalytic medium such as charcoal, powdered pumice, or kieselguhr, and the method of impregnating the medium with the metal forms the subject matter of numerous patents. In Crosfield's process (Eng. Pat. 30282, 1910) an inert medium, such as asbestos or kieselguhr, is impregnated with a solution of nickel sulphate, and then treated with a solution of an alkali hydroxide. The mass, which now contains nickel hydroxide, is washed, dried, and heated in a current of hydrogen, and the resulting product should contain about 30 p.c. of metallic nickel.

Kayser (U.S. Pat. 1004034, 1911) saturates the porous medium with a solution of a nickel salt, and incorporates it in molecular proportions with powdered sodium carbonate. The mixture is then treated with boiling water, dried, and the nickel salt reduced. In a later patent (U.S. Pat. 1001279, 1911) Kayser claims a method of preparing a catalyst which may be exposed to the air for several days without undergoing oxidation and losing its catalytic activity. In this process nickel oxide is reduced at about 500°–600°, and a current of carbon dioxide passed through the material until the gas leaving the apparatus is no longer inflammable.

In order to accelerate the speed of reduction Wilbuschewitsch (U.S. Pat. 1016864, 1911) heats the material in a rotating drum at about 500° in the presence of hydrogen. In a later patent (U.S. Pat. 1022347, 1912) Wilbuschewitz claims a method of recovering spent nickel catalysts, in which the material is first extracted with petroleum spirit, then treated with alkali solution, acidified, treated with sodium carbonate solution, and reduced.

In the case of fats containing substances which act as catalytic poison, Ellis (U.S. Pat. 1078136, 1913) dilutes the material, prior to hydrogenation, with a pure oil or fat. The same inventor claims the use of a catalyst consisting of a porous substance such as 'active charcoal' coated but not materially impregnated with the metallic agent (U.S. Pat. 1060673, 1913).

In Bolton and Lush's process (Eng. Pat. 162382, 1920) the poisoning of the catalyst through the formation of nickel soap is prevented by adding mono- or diglycerides to the oil. These combine with any free fatty acids present and so prevent the nickel being attacked. Bolton has also claimed a method of restoring the activity of the catalyst by washing it in the apparatus, first with hot oil to remove soap and then with a solvent to remove the oil (Eng. Pat. 162370, 1920).

In Higgins' patent (Eng. Pat. 18282, 1912) hydrogenation is accelerated by adding 1–2 p.c of formic or other volatile organic acid to the catalytic material; whilst Lessing (Eng. Pat. 18998, 1912) claims the use of a catalyst composed of nickel carbonyl or other metallic compound which undergoes decomposition at the temperature of hydrogenation.

Reduction of nickel formate in the oil itself is described in a process of Brochet (Bull. Soc. Chim. 1920, 27, 899).

Bedford and Erdmann (Eng. Pat. 27718, 1912) make use of metallic oxides in a form suitable for catalytic agents. They assert (J. pr. Chem. 1913, 87, 425) that nickel oxides are much less sensitive than metallic nickel to external influences, and that they effect more rapid hydrogenation. In the case of the higher oxides of nickel they state that, during the hydrogenation, reduction to metallic nickel does not take place, the reduction stopping at the formation of a nickel suboxide, which is the active catalytic agent. The activity of the catalytic action is increased by the presence of the oxides of other metals. In carrying out the process the oil is heated to 180° in a cylindrical copper vessel fitted with an agitator, while a slow current of hydrogen is passed through it. A small quantity of nickel oxide is introduced, the temperature raised to 255°–260°, and, after the addition of more catalyst, the supply of hydrogen is increased. It is claimed that the hydrogenated product is free from hydroxy acids, and that nickel soap is formed only to a very limited extent.

Erdmann and Rack also attribute any activity of nickel borate to the formation of nickel oxides at 260°. Contrary to the claim of

Schönfeld, they find that nickel borate does not convey hydrogen to unsaturated fats at 175°. Normann, however, attributes the catalytic activity of nickel borate to the formation of metallic nickel reduced by the hydrogen during the hydrogenation process, and finds that there is no positive evidence of the presence of nickel suboxide.

Meigen's experiments (J. pr. Chem. 1915, 92, 390) are also opposed to the views of Erdmann and Bedford, that an oxide or suboxide of nickel is the catalytic agent. He concludes that while it is conceivable that their view may be correct, it is a hypothesis which is lacking in experimental proof.

In Byron's method of preparing a stable catalyst (Eng. Pat. 13382, 1913) the solution of a salt of a catalytically active metal, such as nickel sulphate, is treated with a solution of an alkali silicate, and the precipitate dried, and, if desired, reduced in a current of hydrogen.

Catalysts which do not lose their activity on exposure to the air are prepared by Higgins (Eng. Pat. 23873, 1913) by heating the fatty acid salts of catalytic metals, such as the formates of nickel, cobalt, iron, or copper, until carbonisation begins, preferably in an atmosphere of nitrogen.

Richardson (U.S. Pat. 1151718, 1915) claims the use of an oleate of nickel or other metal; whilst Bacon and Nicolet (U.S. Pat. 1152591, 1915) prepare a catalyst containing nickel hydroxide and aluminium hydroxide, in which the nickel has been rendered active by reduction with hydrogen. Catalysts composed of aluminates of nickel or other heavy metals have also been patented by De Nordiske Fabrike De-no fa Akt. (Eng. Pat. 140371, 1920).

A catalytic agent claimed by Ellis (U.S. Pat. 1156068) is prepared by incorporating hydrated nickel hydroxide $Ni(OH)_2 \cdot H_2O$, with an oily medium, reducing the nickel compound with hydrogen, and removing moisture from the product. In another process, also patented by Ellis (U.S. Pat. 1159480, 1915), a basic compound of nickel is partially reduced with hydrogen to obtain a catalyst consisting of nickel and a lower oxide of nickel.

Other catalysts described by Ellis (U.S. Pats. 1378336–7–8, 1921) are prepared by incorporating organic salts of nickel, etc., with an oily medium, and heating the mixture at reduced pressure; by reducing nickel from nickel oleate in the absence of reducing gases; and by reducing mixtures of metallic salts of nickel, copper and cobalt in an oily medium.

With the object of obtaining a more stable catalyst the Bremen-Besigheimer Oelfabriken (Eng. Pat. 4023, 1915) calcine organic compounds of metals, such as nickel benzoate, either alone or in admixture with carbon or substances containing carbon, until a mixture of the metal or metallic oxides with carbon is obtained. This product is immediately introduced into oil or other inert medium to protect it from atmospheric oxidation. It is claimed that by means of this catalyst oils can be hardened at 150°–200°, whilst the carbon has a deodorising and bleaching effect. In Kimura's process (Eng. Pat. 118323, 1917) a powdered nickel salt is mixed with non-combustible non-catalytic material, such as powdered pumice or asbestos, and the mixture dried and heated in a current of ammonia gas or vaporised ammonium compound such as ammonium chloride. Advantages claimed for the catalysts thus produced are that they act at a relatively low temperature and that any nickel salt can be used in their preparation.

Grote (Seifensied. Zeit. 1920, 47, 713) describes a form of catalyst prepared by treating an aqueous solution of a nickel salt with a solution of an aluminium or magnesium salt, washing the precipitate, and reducing it in hydrogen.

Hydrogen for Catalytic Processes. One of the main essentials for the successful hydrogenation of oils is a supply of pure hydrogen. The gas must be free from sulphur, chlorine, arsenic, and phosphorus, and contain only negligible quantities of oxygen or oxides of carbon.

In some of the larger works (Siemens-Schuckert, Ateliers Oerlikon) a very pure hydrogen, containing as impurity only 0·2 p.c. of oxygen, is prepared by the electrolysis of alkaline distilled water. In other works water gas or producer gas are used as the source of hydrogen. The methods of Linde-Frank-Caro and of the Soc. de l'Air Liquide are based on a fractional distillation of the liquefied components of water gas. The resulting hydrogen is of 97–98 p.c. purity, and is brought to 99–99·5 p.c. by being passed over soda lime heated to 180°.

In Lane's process steam is decomposed by means of reduced iron, and the resulting iron oxide is reduced by the elements of water gas. Spathic iron ore (ferrous carbonate) is used as the original source of iron. This, when heated, yields a porous mass of ferrous oxide, which is packed into a retort, where it is alternately reduced and oxidised. The cost of hydrogen made by this process was about 4*s.* 2*d.* per 1000 cubic feet (Ellis, J. Soc. Chem. Ind. 1912, 31, 1164). Purified water gas is also used by the Soc. Lyonnaise du Gaz and the Griesheim Elektron Co., the decomposition being effected by means of a mixture of lime and iron. These methods yield hydrogen of 97·5–98·5 p.c. purity.

Where petroleum is readily obtainable the method of Rincker-Wolter is used, in which the hydrocarbons of oil gas are decomposed at a high temperature into carbon and hydrogen.

Prior to the war, the relative costs of preparing hydrogen by the different methods were given by Bontoux (Les Matières Grasses, 1914, 7, 4194) as follows: An installation for the production of electrolytic hydrogen cost about £4400 for 1590 cubic feet per hour, and about £9100 for 3530 cubic feet per hour. With electric power at 0·3*d.* per kilowatt-hour the gas cost about 6*s.* 3½*d.* per 1000 cubic feet, including labour. An installation for water gas cost about £7900 for 50 c.m. per hour, and the hydrogen produced cost about 3*s.* 4½*d.* per 1000 cubic feet.

Technology of Hydrogenation. From a consideration of the foregoing outlines of patent processes it will be seen that the main conditions for successful hydrogenation are a suitable temperature, fine state of subdivision of the oil, an active catalyst, and the absence of injurious substances.

Under ordinary atmospheric pressure the temperature most suitable for hydrogenation (over 250°) is liable to cause discoloration of the oil. Hence, in Lane's process, full details of which have been published (Engineer, 1917, 511, 546) a lower temperature is employed (170°–180°) and the pressure increased to about 70–80 lbs. per square inch.

For this purpose the apparatus typified in the patent description (Fig. 2) is constructed as an autoclave, and is surrounded by an outer jacket of firebricks so as to form a flue for heating gases from an external furnace.

The oil is dried first in heating vessels provided with agitators, and subsequently in vacuum pans containing a heating coil and provided with a stirring device.

The mixture of oil and nickel catalyst, which has been prepared as described, is introduced into the top of the autoclave, whilst pure hydrogen is admitted through a pipe at the base. When the gas enters the apparatus the pressure first rises and then becomes stationary at a point depending upon the temperature.

The mass of oil and catalyst is brought into contact with the hydrogen by means of a series of square beaters and cone distributors, and the process is continued until a sample drawn from a tap at the base shows the required degree of hardening.

In practice it has been found that the oil suffers from continual contact with the heated walls of the vessel, and later forms of the apparatus have therefore been constructed with a beater or paddle in the lower part of the vessel.

After sufficient hardening, the oil is drawn off, cooled slightly, and filtered through a press. The residual catalytic material is then washed free from oil, broken up, and prepared for use with a further quantity of oil.

The cost of hydrogenating a ton of linseed oil by means of a plant capable of dealing with one ton per hour was estimated in 1917 at about £2, the main items being the hydrogen (16s.) and loss of catalyst (14s. 2d.).

Properties of Hydrogenated Oils. The degree of hardening depends upon the extent to which the hydrogenation process has been carried, so that products ranging from the consistence of a soft butter to a hard tallow may be obtained from the same oil. In general, the solidified products derived from whale and fish oils are only used for technical purposes such as the manufacture of soap, as claimed by Crosfield and Sons (Eng. Pat. 13042, 1907).

Fish oils and whale oils are deodorised during hydrogenation owing to the conversion of the clupanodonic acid (to which, as Tsujmoto has shown, the odour is mainly due) into stearic acid. To obtain a product yielding a soap in which the odour does not readily reappear it is necessary to continue the hydrogenation until the iodine value is lower than fifty.

Hydrogenated oils are also suitable for use as lubricants, either alone or in admixture with other oils. For edible purposes the chief oils hydrogenated are cotton seed, maize, soya bean, and coconut oils, though any edible oil is suitable for the process. Products such as margarine and artificial lard, which formerly consisted of a vegetable oil mixed with sufficient oleostearin to give a semi-solid mass, are now prepared from an oil such as cotton-seed oil hydrogenated to a sufficient extent to give the required consistence. In the opinion of Ellis (J. Soc. Chem. Ind. 1912, 31, 1165) this method of preparation is preferable to that used by some manufacturers of bleaching hydrogenated oils with untreated oils, since the resulting product has a better flavour and keeps better.

The objection to the use of hydrogenated fish oils or whale oils for food is that the characteristic odours are liable to reappear (Klimont and Mayer, Zeitsch. angew. Chem. 1914, 27, 645), although in other respects they appear to be as digestible as other hardened oils (Offerdahl, *l.c.*).

In Germany, prior to 1914, a technical product termed *candelite* was made from whale oil, and an edible fat *talgol* from vegetable oils, and the factories where the two classes of products were manufactured were kept distinct. With regard to the effect of hydrogenation on oils it has been found that the acid and saponification values are not materially affected, but that the refractive index and iodine value are lowered and the m.p. is raised to an extent corresponding with the degree of hydrogenation. The reduction in the refractive index is shown by the following examples given by Ellis (J. Ind. Eng. Chem. 1914, 6, 117): Maize oil, 1·4514; whale oil, 1·4550; soya bean oil, 1·4538; coconut 'olein,' 1·4425; linseed oil, 1·4610; palm oil, 1·4517; and arachis oil, 1·4547.

The acetyl value of hydroxylated oils such as castor oil is lowered by hydrogenation at the usual temperatures, but Jurgens and Meigen have shown when esters of ricinoleic acid are hydrogenated below 200°, practically only the double bond is saturated.

Experiments on the hydrogenation of cotton-seed oil by Moore, Richter, and Van Ardel (J. Ind. Eng. Chem. 1917, 9, 451) have shown that linolin is hydrogenated more rapidly than olein at 200° and upwards, so that olein tends to accumulate in the fat. To obtain a hardened product with the same iodine value as another but containing, relatively, more saturated glycerides and linolin, it is necessary to effect the hydrogenation under conditions of a lower temperature, greater pressure, more vigorous agitation, and a larger proportion of catalyst.

Marine animal oils yield a much smaller proportion of insoluble bromides after hydrogenation, and the distinctive colour reactions of the original oils are either modified or no longer obtained.

Bellier's reagent (nitric acid sp.gr. 1·4 and resorcinol in benzene) also gives different colour reactions with hardened sesamé, cotton-seed, and arachis oils from those given by the original oils. The Baudouin test for sesamé oil is intensified by hydrogenation, but Halphen's test for cotton-seed oil is inhibited, the chromogenic substance giving the reaction being destroyed after hydrogenation for fifteen minutes with a nickel catalyst at 150°–160°.

The amount of phytosterol is not materially reduced by hydrogenation at 200°, but cholesterol is resinified at 200°, and after treatment at 250° will no longer yield a crystalline derivative (Marcusson and Meyerheim, Zeitsch. angew. Chem. 1914, 27, 201).

Arachidic acid may still be detected in hardened arachis oil, but a modification of the usual test is necessary.

Leimdörfer (Chem. Zentr. 1914, I, 304) has shown that the stearic acid formed in the hydrogenation of oils is chemically identical with natural stearic acid, but that the stearin of hydrogenated oils differs in crystalline form and other physical characters from the stearin of ordinary fats.

Typical hydrogenated oils prepared from whale oil in Germany, and intended as ingredients of margarine, were examined by Sandelin with the following results :—

	Melting point	Solidification point	Acid value	Saponification value	Iodine value	Reichert-Meissl value	Mol. weight of insol. fatty acids	M.p. of the arachidic acid
Original whale oil .	Fluid	Fluid	9·59	192·2	144·8	0·27	287·7	—
Artificial tallow .	47·5°	38·1°	9·88	183·7	56·9	0·25	296·4	75·5°
Artificial stearine . .	54·3	47·3°	7·80	187·7	11·7	0·14	297·0	74·1°
Hydrogenated whale oil	41·9	31·9	5·30	190·9	57·8	0·18	282·0	76·0°

Nickel in Hydrogenated Fats. The presence of trace of the metallic catalyst was at one time f frequent occurrence in hydrogenated fats, es ecially those of continental origin. Thus Bömer (Chem. Rev. Fett Ind. 1912, 19, 221) found ·01 p.c. of ash with 0·006 p.c. of nickel oxide n hydrogenated sesamé oil, and 0·006 p.c. of sh with 0·0045 p.c. of nickel oxide in hardened hale oil. Hence, the detection of nickel in a at indicates the presence of a hardened oil, lthough a negative result in the test does not ecessarily prove that such products are absent, ince means, such as treatment with dilute ydrochloric acid, are often employed to remove he residual metal. In experiments to ascertain he effect of traces of nickel upon the human ystem, Offerdahl (Ber. Deut. pharm. Ges. 1913, 3, 558) found that 0·5 gram of nickel could be aken daily without any injurious effect, 8 p.c. of the metal being rapidly excreted om the system.

For the detection of traces of nickel the imethylglyoxime test may be used (*see* Knapp, nalyst, 1913, 38, 102), but it is necessary to ke into account the fact that certain untreated ls, free from nickel, may show a similar colora- on in this test (Prall). A still more sensitive agent for nickel is *d* benzildiacetyldioxime, s suggested by Atack (Analyst, 1913, 38, 316).

To obtain products relatively free from ickel Ellis (J. Soc. Chem. Ind. 1912, 31, 1165) ys stress upon the importance of using the atalyst in metallic form rather than in the form oxide, since metallic nickel will not readily ombine with free fatty acids to form a soap in e presence of free hydrogen. Too rapid drogenation should also be avoided, so as to event decomposition of the fat, with liberation water, which might cause hydrolysis of the t and liberation of free fatty acids.

For the mechanism of the addition of hydro- n to unsaturated glycerides in the presence of ckel, *see* Thomas (J. Soc. Chem. Ind. xxxix. 20, 10 T.); and for a study of the relation tween the occlusive power of palladium for drogen, and its activity in catalytic hydro- nation, *see* Maxted (Chem. Soc. Trans. 1921, 9, 1281). C. A. M.

HARDWICKIA RESIN *v.* OLEO-RESINS.

HARMALA. The seeds of the wild rue, *Pe- num Harmala* (Linn.), or harmal seeds, have en employed from the earliest times in Eastern medicine as a stimulant, anthelmintic, or even as a narcotic. They are said to be the source of a red dye produced in Southern Russia, and they have been used in the manufacture of oil. Wild rue is an odoriferous herbaceous plant, 1-3 feet high, and inhabits Southern Europe, Asia Minor, Egypt, North-western India, and Southern Siberia (Flückiger, Pharm. J. [iii.] 2, 229).

Harmal seeds contain about 4 p.c. of two alkaloids (probably in combination with phosphoric acid), which are found for the most part in the outer portions of the seed. The first of these, *harmaline* $C_{13}H_{14}N_2O$, was discovered by Göbel (Annalen, 38, 363), the second, *harmine* $C_{13}H_{12}N_2O$, by Fritzsche (*ibid.* 64, 360; J. 1847-8, 639; Annalen, 68, 351; 68, 355; 72, 306; 88, 327; 88, 328; 92, 330; J. 1862, 377), who studied both alkaloids, and obtained numerous derivatives. Fritzsche extracts the seeds with water containing acetic or sulphuric acid, and saturates the solution obtained with common salt, which causes the alkaloids to precipitate in the form of hydrochlorides. The precipitate is dissolved in water, decolorised by treatment with animal charcoal, and the solution obtained is fractionally precipitated by ammonium hydroxide at 50°-60°. The first portion of the precipitate is harmine, and the last portion harmaline. The crude harmaline is best purified by recrystallisation from methyl alcohol (O. Fischer and Täuber, Ber. 18, 400). From methyl alcohol harmaline crystallises in small tables, or from ethyl alcohol in rhombic octahedra. It melts with decomposition at 238°. It is very slightly soluble in cold water or ether, but readily dissolves in hot alcohol. It forms a well-defined crystalline *hydrochloride*

$$C_{13}H_{14}N_2O,HCl.2H_2O\,;$$

hydrocyanide $C_{13}H_{14}N_2O,HCN$; *platinichloride* $(C_{13}H_{14}N_2O,HCl)_2PtCl_4$; *methiodide*

$$C_{13}H_{14}N_2O,MeI\,;$$

chromate $(C_{13}H_{14}N_2O)_2H_2CrO_4$; and *nitro derivative* $C_{13}H_{13}(NO_2)N_2O$. Both the hydrocyanide and the nitro derivative are bases, and combine with acids to form crystalline salts. Nascent hydrogen converts harmaline into a *dihydride* $C_{13}H_{16}N_2O$ (O. Fischer, Ber. 22, 638). Harmaline is shown by Fischer (*ibid.* 28, 2481) to be *dihydro-harmine*, and it can be converted into harmine by oxidation, which is best effected by potassium permanganate in dilute sulphuric acid solution. By oxidation with chromic acid in boiling acetic acid solution or by nitric acid both harmaline and harmine are converted into *harmanic acid* $C_{10}H_8N_2O_4$. By the action of hydrochloric acid on harmaline, Fischer and Tauber obtained a brick-red crystalline powder *harmalol* $C_{12}H_{12}N_2O$, which melts at 212° with decomposition. This compound also occurs naturally in harmal seeds, and has been isolated from them by Fischer (Chem. Zentr. 1901, i 957).

Harmine exists in harmal seeds in much smaller proportion than harmaline. It may, however, be prepared from the latter by simple oxidation, either by the action of heat on the dry chromate, or by heating an alcoholic solution of harmaline nitrate to which hydrochloric acid has been added. Harmine crystallises in four-sided prisms (Schabus, J. 1854, 525). It melts with decomposition at 257°–259°. It is very slightly soluble in water or alcohol, and slightly soluble in ether. The salts of harmine are crystalline and colourless, and in acid solution exhibit an indigo blue fluorescence. The more important are the *hydrochloride*

$$C_{13}H_{12}N_2O,HCl,2H_2O\,;$$

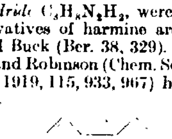
the *platinichloride* $(C_{13}H_{12}N_2O,HCl)_2PtCl_4$; the *methiodide* $C_{13}H_{12}N_2O,MeI$ (F. and T.); and the two *sulphates* $(C_{13}H_{12}N_2O)_2,H_2SO_4,H_2O$, and $C_{13}H_{12}N_2O,H_2SO_4$. Fritszche prepared the following halogen and nitro derivatives of harmine all of which are bases and form crystalline salts. *dichloroharmine* $C_{13}H_{10}Cl_2N_2O$; *nitroharmine* $C_{13}H_{11}(NO_2)N_2O$; *chloronitroharmine* $C_{13}H_{10}Cl(NO_2)N_2O$; and *bromonitroharmine* $C_{13}H_{10}Br(NO_2)N_2O$. A *tetrabromide*

$$C_{13}H_{12}N_2OBr_4$$

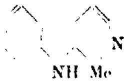
has been obtained by Fischer.

When harmine is treated with concentrated hydrochloric acid at 140°, Fischer and Tauber find that it breaks up into methyl chloride and a new phenolic compound *harmol* $C_{12}H_{10}N_2O$, which crystallises in needles and melts at 321°. When harmol is fused with potash it yields a compound possessing both basic and acid properties, *harmolic acid*, $C_{12}H_{10}N_2O_5$, which melts at 247° (Fischer, Ber. 22, 637). Fischer and Täuber, by acting on harmine in acetic acid solution with chromic acid, obtained dibasic *harminic acid* $C_8H_6N_2(COOH)_2$. It forms silky needles, melting at 345°, at which point it decomposes into carbon dioxide and a crystalline basic sublimate of *apoharmine* $C_8H_8N_2$, m.p. 183°, from which Fischer obtained a well-defined gold salt. A *tetrabromide* $C_8H_8N_2Br_4$, and a *dihydride* $C_8H_8N_2H_2$, were also obtained. Other derivatives of harmine are described by Fischer and Buck (Ber. 38, 329).

Perkin and Robinson (Chem. Soc. Trans. 1912, 101, 1775; 1919, 115, 933, 967) have established the formula



for harmine. In harmaline the pyridine ring contains two, and in tetrahydroharmine it contains four additional hydrogen atoms. Harman, obtained by zinc dust distillation of harmalol, has the formula



and is identical with a base obtained by Hopkins (J. Physiol. 1903, 29, 451) from tryptophane by oxidation; it is further identical with the alkaloid aribine of *Arariba rubra*, Mart. (Spath, Monatsh. 1919, 40, 351).

Harmine and harmaline cause convulsions, increase of saliva, interference with respiration, and depression of temperature in warm-blooded animals (Gunn, T. E. 1910, 47, 245; Flury, Arch. expt. Path. Pharm. 1910, 64, 105). In Turkey peganum seeds are used as an anthelmintic, and Flury (*l.c.*) ascribes this action to the paralysis of the musculature of the parasites caused by harmaline. G. B.

HARMALIN. *Fuchsin* v. TRIPHENYL METHANE COLOURING MATTERS.

HARMALINE, HARMALOL, HARMINE, HARMINIC ACID, HARMOL and **HARMOLIC ACID,** v. HARMALA.

HARTIN v. RESINS.

HARTITE v. RESINS.

HAUERITE. *Manganese disulphide* MnS_2. v. MANGANESE.

HAUSMANNITE. A manganese oxide, Mn_3O_4, crystallised in the tetragonal system, and the richest ore of manganese (Mn 72 p.c.). It forms pyramidal crystals with a good basal cleavage, and with very much the aspect of regular octahedra. They are opaque with a sub-metallic lustre and a dark brownish-black or black colour; the streak is chestnut-brown. Sp.gr. 4·7–4·8; H. 5–5½. Well-developed crystals are found at Ilmenau in Thuringia, Ilfeld in the Harz, Langban in Sweden, Bigrigg in Cumberland, and Miguel Burnier in Brazil. The massive black ores of manganese consist of mixtures of various manganese oxides, and doubtless hausmannite is often present, though not readily recognisable in the massive condition.

L. J. S.

HAÜYNITE v. LAPIS-LAZULI.

HAZELINE. Trade name for a fragrant essence obtained from the fresh bark of *Hamamelis virginiana* (Linn.) or witch-hazel. Is probably analogous to eucalyptol. Is a colourless oil, possessing a pleasant pungent smell and sweet astringent taste. Is used in the treatment of eczema, ulcers, burns, &c., and as a substitute for arnica.

HAZELNUT OIL. The kernels of the seeds of the hazelnut tree *Corylus avellana* (L.), yield about 55 p.c. of a bright yellow oil having the characteristic odour of the nuts. The oil, which is mainly used as a lubricant for fine machinery, such as watch-springs, is said to be liable to adulteration with olive oil, which it resembles in many of its physical and chemical characters. The following values for genuine specimens of the oil have been recorded: sp.gr. at 15°, 0·9164–0·9170; saponification value, 191·4–193·7; and iodine value, 86·2–90·2. Hazelnut oil behaves like olive oil in the elaidin test, but differs from that oil in its low solidification point (−18° to −20°). The presence of olive oil would, therefore, be suggested by the formation of a deposit on chilling the oil.

C. A. M.

HEATHER or **CALLUNA VULGARIS.** In former times the common heath or heather, until recently named *Erica vulgaris*, was used as a dyestuff for producing a yellow colour on woollen goods (Crookes, Dyeing and Calico Printing, 1874, 511). Although now almost superseded, it was until recently employed in the home industries of outlying districts, such as the Highlands of Scotland. Bancroft (Philosophy of Permanent Colours, 1813, 2, 108) states that all five species of the *erica* or heather found in Great Britain are, he believes, capable of giving yellows much like those obtained from dyer's broom. According, however, to the experiments of J. J. Hummel the *E. tetralix* (bell heather) and *E. cinerea* contain only traces of yellow colouring matter. Leuchs (Farben u. Farbekunde, 2, 320) refers to the tanning property of heather, and notes that the effect resembles in character that given by oak bark. H. R. Procter found it to contain 6·4 p.c. of tannin. The colouring matter was isolated by Perkin and Newbury (Chem. Soc. Trans. 1899, 75, 837) from an aqueous extract of the green portion of the plant, in which it appears only to reside, by precipitation with lead acetate in the usual manner. It proved to be identical with the *quercetin* of quercitron bark. The dyeing properties of heather, though distinctly weaker, are so similar in character to those given by quercitron bark as to require no special description. Experiment showed that 36 parts of the heather were necessary to obtain as good a result as that given by 10 parts of quercitron bark.

A. G. P.

HEAVY SPAR. Native barium sulphate *v.* BARYTES and BARIUM.

HEBBAKHADE *v.* GUM RESINS.

HECLA POWDER *v.* EXPLOSIVES.

HECTINE. Trade name for sodium benzosulpho-*p*-aminophenylarsinate.

HEDERAGENIN, HEDERIC ACID *v.* *Ivy*, art. GUM RESINS.

HEDERIN. A poisonous glucoside $C_{64}H_{104}O_{19}$ found in ivy. Dextro-rotatory $[\alpha]_D = +16·27°$. By hydrolysis yields rhamnose and *hederidine* $C_{26}H_{40}O_4$, crystallising in rhombic prisms, m.p. 324°, and subliming without decomposition. Hederine acts as a powerful cathartic (Houdas, Compt. rend. 128, 1463; Joanin, *ibid.* 128, 1476).

HEDERO-TANNIC ACID *v.* *Ivy*, GUM RESINS.

HEDGE-MUSTARD OIL. An oil manufactured from the so-called hedge-mustard or bank-cresses (*Raphanus Raphanistrum* [Linn.]) cultivated in Hungary, and used as a substitute for rape-seed oil. The oil is brought to the market either by itself or mixed with rape-seed oil, and is occasionally sold under this latter name. The siliquous fruit of the plant mentioned bears little seeds which contain 30–35 p.c. oil. This can be for the most part obtained by pressing. It has a dark olive-green colour, and an odour and taste very similar to rape-seed oil; its density and faculty for saponifying with alkali is also nearly the same, so that it is difficult to recognise it in a mixture of the two oils. Valenta has tested the two oils as regards their behaviour with the usual reagents. On acting upon them with acids of different strength, such as sulphuric and nitric acids, a mixture of these, *aqua regia*, phosphoric acid, &c., as well as with oxidising mixtures, as potassium dichromate and sulphuric acid, or concentrated nitric acid saturated with nitric oxide, various colours are produced with both oils, by the shade and intensity of which they can be fairly readily distinguished. The following reaction is most characteristic for hedge-mustard oil; about 5 grams of the oil are saponified with potassium hydroxide and spirit with warming, and the soap thus obtained is filtered from the unchanged oil, which is golden-yellow, and almost odourless and tasteless. On adding a large excess of hydrochloric acid to the concentrated filtrate, it assumes a distinct green colour if a somewhat large portion of hedge-mustard oil be present (J. Soc. Chem. Ind. 11, 181).

HEDIORITE. Syn. for the lactone of α-glucoheptonic acid.

HEDONAL *v.* SYNTHETIC DRUGS.

HEGONON. A combination of albumose and ammonio-silver nitrate.

HEINTZITE, HINTZEITE, *v.* KALIBORITE.

HELCOSOL. *Bismuth pyrogallate* *v.* BISMUTH, ORGANIC COMPOUNDS OF; and SYNTHETIC DRUGS.

HELIANTHIC ACID $C_{14}H_{18}O_8$. An acid found in sunflower seeds (Ludwig and Kromayer, Arch. Pharm. [ii.] 99, 1285).

HELIANTHIN *v.* AZO- COLOURING MATTERS.

HELICON. Syn. for acetyl salicylic acid.

HELINUS OVATUS (E. Meyer, nat. ord. *Rhamnaceæ*) is a climbing shrub indigenous to S. Africa. According to Goodson (Chem. Soc. Trans. 1920, 117, 140), it contains aconitic acid, quercetin, a saponin, and scyllitol, a substance first isolated from certain plagiostomous fishes, but found also in a number of plant products, *e.g.* acorns of the common oak and the leaves of *Cocos plumosa* and *C. nucifera* (*cf.* J. Müller, Ber. 1907, 40, 1821; H. Müller, Chem. Soc. Trans. 1907, 91, 1767; 1912, 101, 2383).

HELIOCHRYSIN *v.* NAPHTHALENE COLOURING MATTERS.

HELIOTROPE *v.* AZO- COLOURING MATTERS. Quartz.

HELIOTROPINE is a crystalline, volatile, poisonous alkaloid of bitter taste contained in *Heliotropium Europæum* (Linn.), and *H. Peruvianum* (Linn.) (Battandier, Répert de Pharm. 1876, 4, 648). The name is also applied to a perfume (*v.* PIPERONAL).

HELIUM. Sym. He. At. wt. 3·99 (Watson); 4·002 (Heuse); 4·001 (Taylor). This element is the lightest member of the group of inert gases discovered by Rayleigh and Ramsay. Its place in the periodic classification is before lithium.

History.—During the solar eclipse of 1868 Janssen observed in the spectrum of the solar chromosphere a line in the yellow, nearly coincident with the sodium lines D_1 and D_2, which was not attributable to any terrestrial substance. Lockyer and Frankland supposed it to be due to the presence in the sun of a new element to which they gave the name 'helium' (ἥλιος, the sun).

Palmieri (Gazz. chim. ital. 1882, 12, 556) observed that the helium spectrum could be obtained from certain volcanic rocks and lavas.

Hillebrand found that the gas evolved from the mineral *uraninite* gave a fluted spectrum, by him attributed to nitrogen, but afterwards proved to be due to helium (Bull. U.S. Geol. Survey, 1889, 78, 43).

The discovery of terrestrial helium was made by Ramsay when searching for argon, &c., in the gases evolved from the mineral *cleveite*, and its presence in the atmosphere was first noticed by Kayser (Chem. News, 1895, 72, 89), who detected the helium line in the air-spectrum. For a bibliography and account of the earlier investigations on helium, *see* Ramsay, Ann. Chim. 1898, [vii.] 13. A classified bibliography of the literature of helium has been compiled by E. R. Weaver, of the American Bureau of Standards (J. Ind. Eng. Chem. 1919, 11, 682). Soddy, in 1903, showed that helium is formed by the disintegration of radio-active bodies (*v. infra*).

Occurrence.—It is now known that helium is very widely distributed, though it occurs only in minute quantities. It is present in air in the proportion of 0·000056 p.c. by weight or 0·00040 p.c. by volume, *i.e.* about 1 volume of helium in 250,000 vols. of air (Ramsay, Proc. Roy. Soc. 1908, 80, A, 599). Helium also occurs in many minerals, of which the chief are *cleveite*, *brøggerite*, *samarskite*, *uraninite*, and *fergusonite*, and it has been detected in the gases of many mineral springs, *e.g.* Bath; in those of the Pyrenees (Bouchard, Compt. rend. 121, 392); of Wildbad (Kayser, Chem. Zeit. 19, 1549); and of Maizières, the gas from the latter containing 5·34 p.c. of helium (Moureu, Compt. rend. 121, 819).

The gas obtained from minerals usually consists principally of helium with about 10 p.c. of nitrogen and smaller amounts of argon, &c. In view of the chemical inertness of helium it is of interest to know in what state it exists in minerals. Ramsay and Travers have found that, by the action of heat alone, almost exactly half the total helium in the mineral is evolved, whilst by heating with sulphuric acid the whole is obtained. The evolution of gas is also in some cases accompanied by an evolution of heat, suggesting that the helium is present as an endothermic compound (Proc. Roy. Soc. 1898, 62, 325). Gray has investigated the conditions under which helium is liberated on grinding minerals, and finds that its evolution begins when the particles have a diameter of 10μ and attains a practical limit when the diameter is 3μ, 28 p.c. of the helium content being then liberated. He concludes that the helium is contained in a structure which is large compared with the molecular structure (Proc. Roy. Soc. 1909, 82, A, 301).

Strutt has investigated the accumulation of helium in rocks in geological time (Proc. Roy. Soc. 1908, 81, A, 272), and concludes that it is due to unknown favourable circumstances, as the rate of loss of helium from minerals under experimental conditions is much greater than the rate of production from radioactive emanations (*v.i.*) (Proc. Roy. Soc. 1909, 82, A, 166).

Helium occurs in the natural gas of Kansas and of Fort Worth, Texas: 1·84 p.c. was found in the gas at Dexter, Cowley Co. (Cady and McFarland, J. Amer. Chem. Soc. 1907, 29, 1523). A plant was erected at Calgary (Canada) for the separation of helium from the natural gas of the Alberta fields. During the European War about 200,000 cubic feet of helium were produced in the United States. The gas contained 92·5 p.c. of pure helium. It was stored in steel cylinders at a pressure of a ton per square inch. Each cylinder containing 200 cubic feet when exposed to atmospheric pressure (Chem. Abst. Amer. Chem. Soc. 1919, 13, 2258). For a description of the mode of extraction and purification, *see* McLennan (Chem. Soc. Trans. 1920, 117, 923). It has also been found occluded in meteoric iron (Ramsay and Travers, Proc. Roy. Soc. 60, 442).

The following table of mineral springs from which gas, containing a large percentage of helium, is evolved, is given by Moureu and Lepape (Compt. rend. 1912, 155, 197):—

Location of Spring	Helium p.c. in natural gas	Yield in litres per year of	
		Natural gas	Helium
Santenay (Côte-d'Or)			
Source Lithium . .	10·16	51,000	5182
„ Carnot .	9·97	170,000	17,845
„ Fontaine-Salée	8·40	—	—
Maizières (Côte-d'Or)			
Source Romaine . .	5·92	18,250	1080
Grisy (Saône-et-Loire)			
Source d'Ys . .	2·18	—	—
Bourbon Lancy (Saone-et-Loire)—			
Source du Lymbe .	1·84	547,500	10,074
Néris (Allier)—			
Source César . .	0·97	3,504,000	33,990
La Bourboule (Puy-de-Dôme)—			
Source Choussy . .	0·1	30,484,800	3048

If the helium be assumed to come in the first place from radioactive disintegrations, it may be looked upon either as nascent helium evolved immediately it is produced or as dissolved, or ancient helium evolved by the disintegration of minerals in which it has been absorbed. The quantities are, however, too large for the former view, and it is more probable that the immediate source is dissolved helium. It is to be noted also that most of the above stations, as well as other sources of radioactive gas, are grouped in the neighbourhood of a line drawn through the towns of Moulins, Dijon, and Vesoul (J. Soc. Chem. Ind. 1912, 31, 720).

Preparation and purification.—The preparation of helium always involves its separation from a mixture with nitrogen, argon, krypton, &c. The mixed gases may be obtained by any of the following methods:—

(1) From 'atmospheric' nitrogen, by passing the gas over heated magnesium (Ramsay and Travers, Proc. Roy. Soc. 64, 183); or a heated mixture of magnesium and lime (Maquenne, Compt. rend. 121, 1147), when the nitrogen is absorbed and the inert gases can be collected.

(2) By fractional distillation of liquid air, according to the method of Ramsay and Travers (Phil. Trans. 1901, 197, 47). Claude has designed an apparatus for producing considerable quantities of the lighter constituents of the atmosphere (Compt. rend. 1908, 147, 624).

(3) From certain mineral springs (*v.s.*). (For methods of collecting the gases *see* Travers' Study of Gases, chap. iv., and Proc. Roy. Soc. 60, 442.) The gases from King's well, Bath, contain 0·12 p.c. of helium by volume, and have been used as a source of the gas by Rayleigh (Proc. Roy. Soc. 1896, 59, 198), the oxygen and nitrogen being separated as from air. It is calculated that this well produces about 1000 litres of helium annually.

The Wildbad springs contain 0·71 p.c. of helium. For determinations of the amount of helium in various natural gases, *see* McLennan (*l.c.*).

(4) By heating certain minerals alone, or with dilute sulphuric acid or acid potassium sulphate. This is probably the best method of preparing helium, and may be carried out as follows:—

The mineral in fine powder is introduced into a wide tube of hard glass or iron sealed at one end and connected by a rubber joint with a manometer and a reservoir, in which the gas can be collected over mercury. The whole apparatus is completely evacuated and the tube slowly heated to redness. When, after some hours, the evolution of helium becomes very slow, the heating is stopped and the gas is pumped out of the reservoir (Travers' Gases, 111). Fusion with an equal weight of acid potassium sulphate in a hard glass tube gives a larger yield, but much frothing takes place, and a preferable method is to heat with dilute sulphuric acid in an evacuated flask (Travers, Proc. Roy. Soc. 1898, 64, 131). This is a comparatively cheap method of production as 1 gram of cleveite yields over 3·2 c.c. of helium, and a kilog. of the mineral can be obtained for £1.

From the mixture of gases thus obtained pure helium may be isolated by one of the following processes:—

Jacquerod and Perrot have found that quartz is permeable to helium at 1000°–1200°; therefore by surrounding a quartz tube with impure helium at that temperature and pumping away the gas from the interior it can be obtained free from nitrogen and other inert gases (Compt. rend. 1907, 144, 135). Watson has shown that this process is not practicable with some kinds of fused quartz (Chem. Soc. Trans. 1910, 812). Ramsay's method consists in introducing the impure gas into a vacuous tube containing charcoal at the temperature of liquid air (Proc. Roy. Soc. 1905, A, 76, 111). Under these conditions all gases except helium and neon are completely condensed, and the vapour pressure of neon is so much less than that of helium, that by systematic repetition of the process a perfectly pure product can be obtained (Watson, *l.c.*).

For a continuous flow apparatus for the purification of impure helium mixtures, *see* Edwards and Elworthy (Trans. Roy. Soc. Canada, 1919, 13, [iii.] 47). Helium containing at least 12 p.c. of impurity can readily be purified by passing in a continuous stream over charcoal at the temperature of liquid air or oxygen. The helium is not absorbed. The rate of flow can be increased to at least 10 litres per hour without decreasing the efficiency of the absorption. By the use of two or more sets of charcoal tubes in parallel the process may be made continuous, as the charcoal may be revivified without disturbing the flow.

Properties.—Helium has so far resisted all efforts to cause it to combine with other elements. It appears, however, to be absorbed to some extent by the finely divided platinum deposited on the walls of a vacuum tube with platinum electrodes by the continued passage of an electric discharge (Travers, Proc. Roy. Soc. 60, 449). This affords a method of separating small amounts of helium and argon, as the latter is only slightly absorbed under these conditions. Cooke has found that zinc vaporised in helium has a vapour density 12 p.c. greater than when vaporised in nitrogen at the same temperature (Zeitsch. physikal. Chem. 1906, 55, 537). This indicates some tendency toward combination.

There is possibly some connection between the chemical inertness of the gas and the fact that its molecules are monatomic as shown by determinations of the ratio of the specific heats. Behn and Geiger, using a modification of Kundts' method, have found the value $C_p/C_v = 1{\cdot}63$, which agrees with that required by theory and found experimentally in the case of other monatomic gases, *e.g.* mercury (Ber. deut. phys. Ges. 1907, 5, 657).

The following determinations of the density of helium have been made (O=16):—

Ramsay and Travers (Phil. Trans. 1901, 197, 47)	D=1·98
Olzewski (Ann. Physik. 1905, [iv.] 17, 997)	D=2·00
Schierloh	D=1·985
Onnes (Leyden, Comm. 1908, No. 108)	D=2·02
Watson (Chem. Soc. Trans. 1910, 97, 827)	D=1·997

According to Heuse (Ber. deut. phys. Ges. 1913, 15, 518), the weight of a normal litre of helium is 0·17856±0·00008 gram. It is next to hydrogen the lightest gas known, and may be used for filling balloons for which it is preferable to hydrogen on account of its non-inflammability.

The fact that helium is both non-inflammable, non-explosive, and possesses 92 p.c. of the lifting power of hydrogen, makes it a most suitable filling for airship envelopes. By the use of helium, the engines of airships can be placed within the envelope if desired. A further advantage possessed by helium over hydrogen is that the buoyancy may be increased or decreased at will by heating and cooling the gas by electric or other means, which fact may possibly lead to considerable modifications in the technique of airship manœuvring and navigation. Moreover, the loss of gas from diffusion through the envelope is less with helium than with hydrogen to the extent of about 30 p.c. (McLennan, *l.c.*). Helium may be mixed with hydrogen to the extent of 26 p.c. without the mixture becoming inflammable (Satterly and Burton, Trans. Roy. Soc. Canada, 1919, 13, [iii.] 211; *cf.* Ledig, J. Ind. Eng. Chem. 1920, 12, 1098).

The molecular weight is taken as 4·00, and as the gas is monatomic this is also the atomic weight.

The refractive index of helium is about 1·000035 for the whole of the visible spectrum, the dispersive power being very small (Scheel and Schmidt, Ber. deut. Phys. Ges. 1908, 6, 207; Hermann, *ibid.* 1908, 6, 211, 246). The accurate value of μ for the D lines is 1·00003500 (Burton, Proc. Roy. Soc. 1908, A, 80, 390; Cuthbertson and Metcalf, *ibid.* 411).

Helium is diamagnetic (Tanzler, Ann. Physik. 1907, [iv.] 24, 931). Its coefficient of solubility in water is less than that of hydrogen, being 0·00967 at 0°, 0·00996 at 20°, and 0·0108 at 50° (Antropoff, Zeitsch. Elektrochem. 1919, 25, 269). Helium resembles hydrogen also in that the product of pressure and volume increases with the pressure, and it is therefore used in thermometry at low temperatures.

Iron, platinum, palladium, and platinum-iridium are all impervious to helium at temperatures up to 1500° (Dorn, Phys. Ztg. 7, 312). The spectrum of helium is characterised by the presence of a strong line, D_3, in the yellow ($\lambda = 5876$), which has been shown to be double, and a bright-green line ($\lambda = 5016$) (*cf.* Stark, Ber. Deut. phys. Ges. 1914, 16, 468). The colour of the glow given by the gas in a Plücker's tube varies with the pressure, being yellow at 7 mm. and green at 1-2 mm. pressure, according to the strength of one or other of these lines. This phenomenon led Runge and Paschen to assume that helium consists of two components (Nature, 1895, 52, 520). This idea has been disproved by subsequent experiments (Nature, 1897, 56, 380).

After many fruitless attempts helium was first liquefied by Onnes (Proc. K. Acad. Wetensch. Amsterdam, 1909, 11, 168; Compt. rend. 147, 421), who found that when cooled in solid hydrogen it gave the Joule-Kelvin effect on expansion through a small nozzle and could therefore be liquefied by the Linde process. From 200 litres of the gas he thus obtained over 60 c.c. of liquid helium in 3 hours.

It is a colourless mobile liquid of density 0·122, being thus the lightest liquid known. It boils at 4·5° absolute, and has a critical temperature about 5° absolute, with a critical pressure of 2·75 atmospheres. By the rapid evaporation of liquid helium a temperature within 1° or 2° of the absolute zero has been reached, but there was no indication of the formation of the solid (Onnes, Proc. K. Acad. Wetensch. Amsterdam, 1909, 12, 175; *ibid.* 1911, 14, 678). Liquid helium has a point of maximum density in the neighbourhood of 2° absolute (Onnes, Communication from Phys. Lab. of Leyden, No. 119).

A method has been described by Bordas (Compt. rend. 1908, 146, 628) for the detection of small amounts of helium by means of a Plücker tube connected with a Dewar tube containing charcoal (Dewar, Proc. Roy. Soc. 1904, 74, 127).

Methods of determining small amounts of helium and hydrogen in air by means of the Jamin interferometer have been described by McLennan and Elworthy (Trans. Roy. Soc. Canada, 1919, 13, [iii.] 19). For the application of the catharometer for the estimation of the helium content in a mixture of gases, *see* Murray (*idem.* 1919, 13, [iii.] 27).

Tschermak has suggested the use of a vacuum tube containing helium as a standard in spectroscopy, and as a source of light in determining refractive indices, &c. (Chem. Soc. Abstr. 1902, ii. 189). Collie has found that the spectrum of helium is considerably modified by the presence of mercury vapour and recommends a helium-mercury tube containing a trace of hydrogen as a standard in spectroscopy (Proc. Roy. Soc. 1902, 71, 25).

Production of helium from radioactive elements.—The gas evolved from a solution of radium bromide is a mixture of oxygen and hydrogen with a radioactive emanation, which can be obtained pure by condensation at a low temperature. When volatilised into a closed space the emanation phosphoresces and gives a characteristic spectrum, but in the course of about four days the radioactivity disappears and the spectrum changes to that of helium (Ramsay and Soddy, Proc. Roy. Soc. 1903, 72, 204; 1904, 73, 346). During this change the volume increases to three times that of the original emanation (Dewar and Curie, Compt. rend. 1904, 138, 190; Indrikson, Physikal. Zeitsch. 1904, 5, 214; Himstedt and Meyer, Ann. Physik. 1904, 15, 184).

It is probable that helium is the final product of the disintegration of radium. The rate of production of helium is 0·37 cub. mm. per day from 70 mgm. of radium chloride, and agrees with that calculated by Rutherford on the assumption that α-particles are helium atoms carrying two ionic charges (Dewar, Proc. Roy. Soc. 1908, 81, A, 280).

Helium is also a product of the disintegration of actinium (Giesel, Ber. 1907, 40, 3011), and of thorium radioactivity (Strutt, Proc. Roy. Soc. 1907, 80, A, 56). The rate of production in this case also supports the view that the α-particle is identical with the helium atom (Soddy, Phil. Mag. 1908, [vi.] 16, 513; Physikal. Zeitsch. 1909, 10, 41).

HELKOMEN. Trade name for a basic bismuth dibromohydroxynaphthoate. Yellow odourless powder. Used as a substitute for iodoform.

HELLANDITE. Silicate of yttrium, erbium, calcium, aluminium, and manganese crystallised in the monoclinic system. One analysis showed Y_2O_3 19·29, Er_2O_3 15·43, Ce_2O_3 1·01 p.c. The crystals are prismatic in habit, and when fresh are nut-brown in colour with a resinous lustre on the conchoidal fracture. Sp.gr. 3·70; H. 5½. The mineral is readily soluble in hydrochloric acid with evolution of chlorine, and it is fusible in the Bunsen flame. Usually, however, it is much altered to a yellow or white earthy material which is optically isotropic and contains much water. The crystals are found singly, in association with tourmaline, apatite, thorite, orthite, &c., embedded in the granite pegmatite-veins which are quarried for felspar in the neighbourhood of Kragerö in the south of Norway.

L. J. S.

HELLEBOREIN, HELLEBORIN, HELLEBORESIN, HELLEBORETIN, *v.* BLACK HELLEBORE ROOT.

HELL-HOFFITE *v.* EXPLOSIVES.

HELMITOL. Trade name for a compound of hexamethylenetetramine (urotropine) and anhydromethylene citric acid. Known also as neurotrophine and uropurgol. A mixture with hetraline forms citramine or citraminoxyphen (*v.* SYNTHETIC DRUGS).

HEMELLITHENOL *v.* PHENOL AND ITS HOMOLOGUES.

HEMIMORPHITE (or Electric Calamine). Hydrous silicate of zinc, $H_2Zn_2SiO_5$, crystallising in the orthorhombic system, and an important ore of zinc. The water is expelled only at a red heat, and the formula may be written as an acid salt or as a basic metasilicate $Zn_2(OH)_2SiO_3$, or as a basic diorthosilicate $H_2Zn_2(ZnOH)_2(SiO_4)_2$. An important chemical character, of help in recognising the mineral, is the fact that it readily gelatinises with acids. Crystals are not uncommon, but are usually small; they are often grouped in fan-like aggregates, at the edges of which the perfect prismatic cleavage with pearly lustre may often be seen. When doubly terminated, they show a characteristic hemimorphic development, different kinds of faces being present at the two ends of the vertical axis. Connected with this polarity is the strong pyroelectric character of the crystals. The mineral also forms mamillated and stalactitic masses; or it may be massive and cavernous and cellular, being then often mixed with clayey matter or smithsonite. The colour ranges from white to yellow and brown, and is sometimes bright blue or green. Sp. gr. 3·45; H. 4½–5. Hemimorphite usually occurs in association with zinc carbonate (smithsonite) and zinc blende and ores of lead, often as veins and beds in limestone strata. Fine large crystals are found at Santa Eulalia, Chihuahua, Mexico, and the mineral has been mined as an ore at several localities, *e.g.* Cumberland, Altenberg in Rhenish Prussia, Sardinia, Santander, Hungary, Rhodesia, United States, British Columbia, &c. The ambiguous name calamine (*q.v.*) is often applied to this mineral species.

L. J. S.

HEMIPINIC ACIDS $C_{10}H_{10}O_6$. *n-Hemipinic acid* (3 : 4-*dimethoxybenzene*-1 : 2-*dicarboxylic acid*) is a product of oxidation of narcotine (Wöhler, Annalen, 1844, 50, 17; Blythe, *ibid.* 43); of opianic acid (Beckett and Wright, J. 1876, 806); of berberine (Schmidt, Ber. 1883, 16, 2589); of corydaline (Dobbie and Lauder, Chem. Soc. Trans. 1894, 57; *ibid.* 1895, 18; *ibid.* 1897, 657; *ibid.* 1902, 146; Martindale, Arch. Pharm. 1898, 236, 214); and of other alkaloids. It is prepared by boiling the oxide of opianic anhydride with potassium hydroxide. The solution is then acidified and extracted with ether (Goldschmidt, Monatsh. 1888, 9, 766). It crystallises with ½ and also with 2 molecules of water.

Properties.—Both in the normal and the meta acids the m.p. varies with the rate of heating. When heated rapidly it has m.p. about 181° (Dobbie and Lauder, Chem. Soc. Trans. 1899, 678). It is sparingly soluble in cold water, readily so in alcohol; the aqueous solution gives an orange-yellow precipitate with ferric chloride, and no precipitate with silver nitrate solution. When heated with ammonia it yields an imide $C_{10}H_9NO_4$ (Kühn, Ber. 1895, 28, 809), the potassium salt of which when heated with ethyl iodide at 150° yields the characteristic *hemipinethylimide*; m.p. 92°–96° (Goldschmidt and Ostersetzer, Monatsh. 1888, 9, 762; Liebermann, Ber. 1886, 19, 2282; Freund and Heim, ibid. 1890, 23, 2906). When treated with phosphorus pentachloride at 140° hemipinic acid yields the anhydride, which is also obtained by the action of equal volumes of methyl alcohol and concentrated sulphuric acid on the acid (Beckett and Wright, *l.c.*; Wegscheider, Monatsh. 1897, 18, 649).

The *anhydride* $C_{10}H_8O_5$ forms brilliant needles; m.p. 166°–167°. It reacts with hydroxyquinol, forming *dihydroxydimethoxy fluorescein* (Liebermann and Wolbling, Ber. 1902, 35, 1782), and with resorcinol, forming *dimethoxyfluorescein* (Friedl, Weizmann, and Wyler, Chem. Soc. Trans. 1907, 1584).

Lagodzinski has synthesised alizarin from hemipinic acid by treating the latter with benzene in the presence of aluminium chloride. The aluminium compound so formed is decomposed with hydrochloric acid, and the resulting product $C_{15}H_{12}O_5,H_2O$ is dissolved in cold sulphuric acid and heated to 100°. The violet solution is poured on to ice and the mono-methyl ether of alizarin so obtained is decomposed with hydrogen iodide (Ber. 1895, 28, 1427).

The *methyl ester* exists in 2 modifications; m.p. 121°–122° and 138° respectively, the latter being the more stable form at ordinary temperature (Wegscheider, Monatsh. 1897, 18, 418, 589, 629).

Other esters (Wegscheider, *l.c.*; Monatsh. 1902, 23, 327, 381; Landau, Ber. 1898, 31, 2090; Cahn-Speyer, Monatsh. 1907, 28, 803); a number of metallic salts (Salzer, Ber. 1897, 30, 1102), and many other derivatives have been obtained (Goldschmidt, Monatsh. 1887, 8, 512; Mealen, Rec. trav. chim. 1896, 15, 282, 323; Claus and Predari, J. pr. Chem. 1897, [ii.] 55, 171; Besterzycki and Fink, Ber. 1898, 31, 930; Wegscheider, *l.c.*, and Monatsh. 1903, 24, 375; Dobbie and Lauder, *l.c.*, amongst others).

On gentle nitration, hemipinic acid yields chiefly nitro derivatives, but on more energetic nitration 5 : 6-dinitro-2 : 3-dimethoxybenzoic acid is formed (Wegscheider, Monatsh. 1908, 29, 54, 557; *ibid.* 1910, 31, 709).

m-Hemipinic acid (4 : 5-dimethoxybenzene-2 : 3-dicarboxylic acid) is a product of the oxidation of papaverine (Goldschmidt, Monatsh. 1885, 6, 380); of laudanin (*ibid.* 13, 695); and of corydic acid (Dobbie and Marsden, Chem. Soc. Trans. 1897, 664). It is also obtained by the oxidation of trimethylbrazilin (Gilbody, Perkin, and Yates, Chem. Soc. Trans. 1901, 1400; *ibid.* 1902, 1045); of tetramethylhæmatoxylin (*ibid.* 1061); and of 4 : 5-dimethoxy-*o*-toluic acid (Luff, Perkin, and Robinson, *ibid.* 1910, 1136). It can be prepared according to the following method:—

5 : 6-Dimethoxy-1-hydrindone (3 grams) is boiled with nitric acid (12 grams) and water (36 c.c.). The clear yellow solution is neutralised with sodium carbonate, mixed with hydrochloric acid until the solution turns Congo paper blue, evaporated to dryness, the residue mixed with sand and extracted in a Soxhlet apparatus with ether. The ethereal solution is dried over anhydrous sodium sulphate, evaporated, and the residue dissolved in hot water, and after digestion with animal charcoal and filtration, the solution is allowed to evaporate slowly in the air. It can also be obtained by the oxidation of *iso*-nitrosodimethoxyhydrindone with potassium permanganate, which gives an almost theoretical yield (Perkin and Robinson, Chem. Soc. Trans. 1907, 1083) and by heating aqueous dimethoxycarboxybenzoyl formic acid (Perkin, *ibid.* 1902, 1025; *see* also Perkin and Yates, *ibid.* 242).

m-Hemipinic acid crystallises with 1 and with 2 molecules of water, has m.p. about 199° (Dobbie and Lauder), and is much less soluble in water than the normal acid. Its aqueous solution gives a cinnabar orange precipitate with ferric chloride and a white precipitate with silver nitrate. On heating it forms an anhydride, m.p. 175°; when fused with potash it yields protocatechuic acid and carbon dioxide. When treated with nitric acid it gives dinitroveratrol, whilst on reduction it yields 4 : 5-dihydroxyphthalic acid (Rossin, Monatsh. 1891, 12, 488). Its *ethylimide* has m.p. 228°–230°, and unlike that from the normal acid, it is very sparingly soluble in methyl alcohol. The ethyl esters have been prepared by Rossin (*l.c.*)

HEMISINE. Syn for Adrenaline (*q.v.*); also SYNTHETIC DRUGS.

HEMLOCK SPRUCE RESIN *v.* RESINS.

HEMP. The name of various plants and of the fibres derived from them (*see* also BAST-FIBRES). The following list embraces these fibres under their commercial denominations, with the names of the plants which produce them:—

Common hemp . .	*Cannabis sativa* (Linn.).
African bowstring hemp .	*Sanseviera guineensis* (Willd.) and others
Bastard hemp . .	*Datisca cannabina* (Linn.).
Bengal or Bombay hemp .	*Crotalaria juncea* (Linn.).
Bombay hemp (also) .	*Hibiscus cannabinus.*
Bowstring (of India) hemp	*Sanseviera Roxburghii* and others.
Bowstring (of India) hemp (also)	*Calotropis gigantea* (Dryand.).
Brown hemp . . .	*Crotalaria juncea* (Linn.).
Brown (Indian) hemp (also)	*Hibiscus cannabinus* (Linn.).
Florida bowstring hemp .	*Sanseviera longiflora* (Sims).
Indian (in America) hemp	*Apocynum cannabinum* (Linn.).
Jubbalpore hemp . .	*Crotalaria juncea* (Linn.).
Madras hemp . . .	*Crotalaria juncea* (Linn.).
Manilla hemp . . .	*Musa textilis.*
Sisal hemp . . .	*Agave rigida* (Mill.).
Sunn hemp . . .	*Crotalaria juncea* (Linn.).
Virginian or Water hemp.	*Acnida cannabina* (Linn.).

Of these, *Cannabis sativa*, nat. ord. *Urticaceæ*, allied to the hop plant, furnishes the true hemp. The plant is an annual, growing ordinarily to the height of 8 or 10 feet, but sometimes exceeding that limit by several feet; and it doubtless owes its origin to some part of temperate Asia. On extending its habitat, the character of the plant changed with soil and climate, giving origin to the supposed varieties *C. chinensis* and *C. indica*, the former of which is cultivated for its bast-fibres (hemp), while the latter is grown for its narcotics.

Hemp fibre examined by the microscope resembles that of flax in being round and ribbed; it has a mean diameter of 0·2 mm., and exhibits small hairy appendages at the joints. According to Haberlandt, the breaking strain of a cord of 1 sq. mm. section is on the average 34·5 kilos. In *Manilla* hemp the fibrous bundles are oval, nearly opaque, and surrounded by a number of rectangular cells composing a dried tissue. The bundles are smooth. *Sisal* hemp forms oval fibrous bundles surrounded by cellular tissue; a few smooth ultimate fibres projecting from the bundles. It is more translucent than Manilla, and is characterised by the large quantity of spiral fibres in the bundle.

Hemp is cultivated (1) for its fibre; (2) for its resin; (3) for the oil contained in its seed; (4) for the seed itself. The tough, elastic, and durable fibre is better adapted for the manufacture of cordage and sail-cloth than any other known material. It is, moreover, employed for canvas, tarpaulin, and towelling. The finest qualities for these purposes are imported from Italy and Russia. The preparation of the fibre is similar to that of flax; the stems being bruised and 'retted' or fermented in water, after which they are again beaten out and finally 'scutched' and 'hackled' or combed (*v.* FLAX). The water in which hemp has been steeped produces no evil effects on the health of a district when allowed to flow into running water, but it always destroys the fish together with certain vegetable growths (Renouard, Bied. Zentr. 1880).

The resin of hemp is employed in India as *charas*, *bhang* or *siddhi*, and *gánjá*, in which form it is used for its intoxicating and narcotic properties. *Charas* is the resin itself; *bhang* or *siddhi* consists of the dried resinous leaves and stalks; it is used for smoking, for making sweetmeats along with honey and sugar, or for forming a potable infusion. *Gánjá* is composed of the resinous fruiting heads of the female plant and is similarly employed. In 'A Report on Indian Fibres and Fibrous Substances,' Spon, 1887, it is stated that *Cannabis sativa* (var. *indica*) is chiefly, if not exclusively, cultivated on account of its narcotic principle. It has been found that the narcotic-yielding plant affords only a worthless fibre, and it is presumed that the climate of India favours the production of narcotic at the expense of the fibre. To attempt an extension of its cultivation, fiscal difficulties of a very formidable character would also have to be overcome, for the Government of India would never permit a plant of which the leaves and flowers yield so pernicious a narcotic to be widely grown. According to Hunter (The Indian Empire, and its People, History, and Products, 2nd ed. 455), excise duties are levied upon these resinous products; the hemp which furnishes them is chiefly confined to a limited area in Rájsháhí district, Bengal, and to the inner valleys of the Himalayas. The use of them is a frequent cause, not only of crime, but also of insanity. Government attempts to check consumption—first, by fixing the retail duty at the highest rate that will not encourage smuggling; and secondly, by continually raising that rate as experience suggests.

The effect of hemp-resin and its compounds on the consumer is at first to exhilarate and to promote appetite. Further doses produce delirium, sleep, and sometimes catalepsy.

Hemp-resin examined by T. and H. Smith is soluble in alcohol, and has a warm, bitter, acrid taste with a slight odour. It melts between 70°

and 90°, and has a pale-brown colour. It is called *cannabin*.

The oil is obtained by expression from the seed, which yields from 25 to 30 p.c. of oil, and 70–75 p.c. of residual cake used for cattle feeding, although sparingly on account of its laxative properties.

The seeds themselves are used as food for birds, some kinds of which are inordinately fond of them. They are roundish, ovate, of a grey colour, and contain 34 p.c. of oil and 16 p.c. of albuminoids.

The essential oil of *C. sativa* was prepared by L. Valenta (Gazzetta, 10, 479–481) by distilling the fresh leaves with water and agitating the resulting milky distillate with ether. The oil dried over calcium chloride and distilled repeatedly from sodium is colourless and mobile (b.p. 256–258°). The analysis agreed with the formula $C_{15}H_{24}$; the vapour density could not be determined, as it decomposes at 300°. The essential oil mixes in all proportions with alcohol, ether, or chloroform.

HEMP SEED OIL. The hemp plant, *Cannabis sativa* (Linn.), is cultivated in France, Belgium, Germany, Northern Italy, Algeria, North America, India, Manchuria, and Japan. A large quantity of the seed is still grown in France, where the oil is expressed for commercial purposes. The seeds yield about 33 p.c. of oil. The colour of the freshly-expressed oil is light green to greenish yellow, which becomes brownish-yellow on keeping.

Hemp seed oil contains a few p.c. of solid glycerides, most likely palmitin, with a small amount of stearin or arachin. The liquid fatty acids in hemp seed oil consist of linolic acid, and smaller quantities of oleic, and linolenic (and isolinolenic (?)) acids.

Hemp seed oil is used as a paint oil, though less frequently in this country than on the Continent. Considerable quantities are used on the Continent for making soft soap, characterised by a dark green colour. The lower qualities of hemp seed oil are stated to be used in the manufacture of varnishes.

It is sometimes used as an adulterant of linseed oil, and may also be present accidentally, owing to admixture of the seeds prior to expression.

The following values have been recorded for genuine samples of hemp seed oil: Sp.gr. 15°/15°, 0·9280–0·9283; saponification value, 190–192; iodine value, 157–166; m.p. of fatty acids, 17°–21°. The presence of hemp seed oil in linseed oil would be indicated by the lower iodine value, and lower yield of insoluble bromides. J. L.

HENBANE. *Hyoscyamus. Jusquiame*, Fr.; *Bilsenkraut*, Ger.

Henbane, *Hyoscyamus niger* (Linn.) (Bentl. a. Trim. 194), is one of the group of poisonous plants belonging to the natural order *Solanaceæ* and is nearly related to belladonna, stramonium, and duboisia. It has been employed in medicine since the 7th century and an allied species, having similar properties, *H. albus* (Linn.) was known to Dioscorides. There are two varieties of *H. niger*, one an annual and the other a biennial. Both are to be obtained in the market, but the leaves or green tops of second-year plants of the biennial variety are the official variety and should alone be employed in medicine (*Hyoscyami folia*, B.P.; *Hyoscyamus*, U.S.P.). The seeds possess still greater activity, but they are only used in the manufacture of alkaloid. Henbane is a coarse hairy erect herb with pale-yellow flowers marked with purple veins, and the whole plant evolves an unpleasant odour. It occurs wild throughout Britain and most parts of Europe, Asia, and Northern Africa, and has been naturalised in North and South America. Henbane is employed as a sedative, anodyne, or hypnotic, and, like belladonna and stramonium, it dilates the pupil of the eye. Its activity is destroyed by the presence of free alkali, with which it should therefore not be administered (Garrod, Pharm. J. 17, 462; 18, 174).

The active constituents of henbane are two alkaloids. The one, *hyoscyamine* $C_{17}H_{23}NO_3$, was first obtained in a pure state by Geiger and Hesse (Annalen, 7, 270) and more completely studied by Hohn and Reichardt (Annalen, 157, 98); the other, present in much smaller proportion, *hyoscine* $C_{17}H_{21}NO_4$, was discovered by Ladenburg (Annalen, 206, 282). The sulphate of the former and the hydrobromide of the latter are official in the B.P. The U.S.P. has hyoscyamine hydrobromide and scopolamine (= Hyoscine) hydrobromide. The alkaloidal content of the dried leaves is very variable; in the B.P. drug 0·045–0·14 p.c.; in annual plants from Southern Europe, 0·03 p.c.; in isolated cases yields up to 0·27 p.c. have been reported (B.P. Codex). The U.S.P. demands a minimum of 0·065 p.c. The seeds contain 0·5–0·6 p.c. of alkaloid. Hyoscyamine also occurs together with atropine in belladonna and stramonium (*v.* STRAMONIUM), and 'duboisine,' the alkaloid of *Duboisia myoporoides* (R. Br.), is identical with hyoscyamine (Ladenburg and Petersen, Ber. 20, 1661). Both hyoscyamine and hyoscine, like atropine, are mydriatic alkaloids.

To obtain hyoscyamine from henbane seeds Hohn and Reichardt first deprive them of fixed oil by treatment with ether and then exhaust by means of alcohol acidified with sulphuric acid. The clear extract, after removal of the alcohol by distillation, is almost neutralised by soda and precipitated with tannic acid. The moist precipitate is mixed with lime and extracted with alcohol. The alcoholic solution is acidified, concentrated, and purified by washing with ether. The alkaloid is then set free by the addition of soda and isolated by extraction with ether. Other somewhat similar methods have been suggested by Rennard (Neues Rep. Pharm. 17, 91), Thorey (Pharm. J. [iii.] 12, 874), and Thibaut (Chem. Zentr. 1875, 565). Duquesnel (J. Pharm. Chim. [v.] 5, 131) extracts the seeds with hot 90 p.c. alcohol containing tartaric acid, and from the solution obtained removes the alcohol by distillation. There remains a residue of two layers, a lower syrupy and an upper oily layer, which latter is found to contain most of the alkaloid, perhaps in combination with a fatty acid. This is extracted by treating the oil with water acidified with sulphuric acid. The solution is nearly neutralised with potassium bicarbonate, concentrated to a syrup, and extracted with alcohol, which leaves potassium sulphate undissolved. The alcohol is removed from the solution by distillation, and the residue, diluted with water and treated with a slight excess of potassium bicarbonate, is extracted with chloroform. The crude hyoscyamine is removed from the chloroform solution by water acidified with sulphuric acid, is purified by treatment with animal charcoal, and the solution is then concentrated to a syrup. The alkaloid is set free by an excess of calcium carbonate, and mixed with sand, is dried over sulphuric acid. Finally, treatment with chloroform extracts the hyoscyamine and yields it on evaporation in prismatic needles.

For the properties and reactions of hyoscyamine and atropine *v.* TROPEINES.

Brandes, who analysed henbane seeds, found 24 p.c. of *fixed oil* (Berz. J. 21, 180): a substance 'hyoscypicrin,' supposed to be a glucoside, was obtained by Hohn and Reichardt, and the presence of potassium nitrate in the leaves was pointed out by Thorey and in the medicinal extract by Attfield (Pharm. J. 3, 447).

Hyoscyamus muticus (Linn.), a species of henbane occurring in certain parts of India, and particularly in Egypt and the Soudan, has been examined by Dunstan and Brown (Chem. Soc. Trans. 75, 72), who find hyoscyamine to be the only alkaloid present in any notable quantity. It may be distinguished from *H. niger* by the occurrence of characteristic, branching, non-glandular hairs on the stem and leaves. *Hyoscyamus muticus* from Egypt has of late years become the principle industrial source of hyoscyamine (atropine). G. B.

HENDECATOIC or **UNDECATOIC ACIDS**

$C_{11}H_{22}O_2$

1. *n-Undecylic acid* $CH_3[CH_2]_9COOH$ is a crystalline solid having a faint smell of caproic acid; it is obtained by the reduction of undecylenic acid or by the oxidation of methylundecylketone; m.p. 28·5°; b.p. 228° (160 mm.) (Krafft, Ber. 1879, 1664).

2. *Methyl dibutyl acetic acid*

$$[C(CH_3)_3]_2C(CH_3)COOH$$

is obtained with other products by the oxidation of *iso*tributylene. A white crystalline solid, insoluble in water, but soluble in alcohol or ether; m.p. 66°–70°; b.p. 260°.

3. *Umbellulic acid* $C_{11}H_{22}O_2$. The nuts of the Californian bay tree (*Umbellularia Californica* [Nutt.]) contain about 60 p.c. of a fat easily soluble in ether. It is a white, hard, tallowy mass m.p. 31°. By saponification with caustic potash and decomposition with hydrochloric acid, the acid is obtained as a white solid with a faint odour and very disagreeable and irritating taste; m.p. 31°–34°; b.p. 275°–280°. Its alkyl esters are colourless mobile liquids of agreeable odour (Spillman and O'Neill, Amer. Chem. J. 1882, 206). Possibly identical with *cocinic acid* found by Saint-Evre in cocoa-nut oil, and with the *undecylic acid* of Krafft (*v. supra*).

HENDECENOIC ACID, $C_{11}H_{20}O_2$, an acid boiling at 258°–261° found in petroleum; known also as *petrolcumic acid*. It is obtained from the petroleum distillate, b.p. 250°–270°, by adding sodium hydroxide and then to the alkaline extract, sulphuric acid. This is treated with alcohol and hydrochloric acid, and the resulting ester fractionated and hydrolysed with alcoholic potash (Hell and Medinger, Ber. 1874, 1217; 1877, 451).

HENNA (*Al-henneh, Al-henna,* or *All-Kenna*). The root and leaves of *Lawsonia alba*, an aqueous infusion of which has long been used in the East as a prophylactic against certain skin diseases. The root is considered as a specific against leprosy and the flowers are used in preparing a perfume. The fruit is employed as an emmenagogue. Used largely as a dye and for staining the hair, soles of the feet, palms of the hands and nails of an orange-red colour, and to colour the manes and tails of horses.

Lawsone, $C_{10}H_6O_3$, the colouring matter contained in henna leaves is a hydroxy naphthoquinone, and is probably identical with 2-hydroxy-1·4-naphthoquinone. (Tommasi, Gazz. chim. ital. 1920, 50, i. 263) *v.* ALKANET and ALKANNA.

HEPARADEN and **HEPARON** *v.* SYNTHETIC DRUGS.

HEPAR SICC. *v.* SYNTHETIC DRUGS.

HEPATIC CINNABAR *v.* CINNABAR.

HEPTOIC ACIDS $C_7H_{14}O_2$.

1. *n-Heptoic acid, œnanthylic acid*

$$CH_3(CH_2)_5COOH$$

Obtained by the oxidation of œnanthol (Bussy, Annalen, 60, 248; Tilly, *ibid.* 67, 107; Krafft, Ber. 1882, 1717; Schorlemmer and Grimshaw, Annalen, 170, 141); also formed by the oxidation of castor-oil, of oleic acid, and of normal heptyl alcohol (Schorlemmer, Annalen, 161, 279; Tripier, Bull. Soc. chim. [iii.] 11, 99); from the normal hexyl cyanide (Franchimont, Annalen, 165, 237); and by the reduction of dextrosecarboxylic acid (Kiliani, Ber. 1886, 1130). An oily liquid; b.p. 222·4 (743·4 mm.), m.p. −10·5°, sp.gr. 0·9183, 20°/.

2. *isoHeptoic acid*; *α-methylhexoic acid*

$$CH_3[CH_2]_3CH(CH_3)COOH$$

Obtained by boiling hexyl cyanide with alcoholic potash (Hecht, Annalen, 209, 309), or by the reduction of fructosecarboxylic acid (Kiliani, Ber. 1885, 3071). An oily rancid smelling liquid; b.p. 211·5 (745·8 mm.), sp.gr. 0·9138, 21°/.
Soluble in 278 parts water.

3. *Isoœnanthylic acid* found among the products obtained by heating a mixture of sodium acetate and sodium *iso*valerate; b.p. 217°, sp.gr. 0·9260, 15°/ (Poetsch, Annalen, 218, 66).

4. *isoAmyl acetic acid*; *δ-methylhexoic acid*

$$(CH_3)_2CH[CH_2]_3COOH$$

Obtained by the action of sodium and *iso*amyl iodide upon ethyl acetate (Frankland and Duppa, Annalen, 138, 338), or by the distillation of *iso*amylmalonic acid (Paal and Hoffmann, Ber. 1890, 1498); b.p. 208°–210°, sp.gr. 0·9122, 13°/.

5. *Methyl diethyl acetic acid*; *αα-methylethylbutyric acid* $CH_3(C_2H_5)_2C{\cdot}COOH$. Obtained by prolonged heating of methyl diethyl carbinol cyanide with strong hydrochloric acid (Schdanow, Annalen, 185, 120); b.p. 207°–208° (753 mm.); almost insoluble in water.

6. *Methyl isopropyl propionic acid*; *βγ-dimethylvaleric acid*

$$CH_3(C_3H_7)CH{\cdot}CH_2{\cdot}COOH$$

Obtained by heating sodium *iso*valerate with sodium ethoxide in a stream of carbon monoxide (Loos, Annalen, 202, 321); b.p. 220°.

7. *Ethylpropylacetic acid*; *α-ethylvaleric acid* $CH_3(CH_2)_2CH(C_2H_5)CO_2H$. Obtained by hydrolysing ethylpropylacetoacetic ester with alkali (Kiliani, Ber. 1886, 227); b.p. 209·2°.

8. *Active amylacetic acid*; *γ-methylhexoic acid* $CH_3(C_2H_5)CH\cdot CH_2\cdot CH_2\cdot COOH$. Obtained by heating active amylmalonic acid (Welt, Ann. Chim. [vii.] 6, 132); b.p. 221°; sp.gr. 0·9140, 20°/20°.

9. *Methylisobutylacetic acid*; *αγ-dimethylvaleric acid*. Obtained by heating methylisobutylmalonic acid (Burrows and Bentley, Chem. Soc. Trans. 1895, 511); b.p. 204°–205°.

iso-**HEPTYLACETIC ACID** *v.* Nonoic acids.

n-**HEPTYLSUCCINIC ACID**

$$C_7H_{15}\cdot CH(CO_2H)CH_2\cdot CO_2H$$

Obtained by the reduction of hexylita-, -citra- or -mesaconic acids with sodium amalgam (Fittig and Hoefiken, Annalen, 304, 337); m.p. 90°–91°.

HERABOL. *See Myrrh*, art. Gum resins.

HERCULES METAL *v.* Aluminium.

HERCULES POWDER *v.* Explosives.

HERMOPHENYL *v.* Synthetic drugs.

HERNIARINE *v.* Lactones.

HEROIN *v.* Opium and Synthetic drugs.

HERRING OIL is obtained from the several species of herring, *Clupea harengus* (North Sea), *C. Pallasi*, *C.* and *V.* (Japan). This oil is now extracted on a commercial scale in Japan, and genuine specimens of such oil have been prepared by Tsujimoto. The Japanese herring oil yields on brominating 3·82–6·5 p.c. of the octobromide of clupanodonic acid, which is a characteristic constituent of all fish oils. The herring oils produced in Europe (Norway) are not kept separate from other fish oils, and, therefore, do not represent such pure oils as those described by Tsujimoto. The iodine value of genuine herring oil ranges from 103 to 123 (Tsujimoto), whilst the commercial North Sea herring oil has a higher iodine value (about 131–142).

Like all other fish oils, herring oil is chiefly used in the leather industry. J. L.

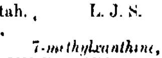
HESPERIDIN *v.* Glucosides.

HESSIAN PURPLE, RED, YELLOW. *v.* Azo-colouring matters.

HESSITE or **TELLURIC SILVER.** Silver telluride, Ag_2Te, crystallised in the cubic system and isomorphous with argentite. The silver (Ag 63·3 p.c.) is often partly replaced isomorphously by gold, forming a passage to petzite. The colour is lead-grey, and the material somewhat sectile; sp.gr. 8·3–8·9, H 2½–3. The best crystals, though much distorted, are from Botes in Transylvania, and massive material was formerly obtained in some quantity in the Slavodinsk mine in the Altai Mountains, Siberia. The mineral has also been found in California, Colorado, and Utah. L. J. S.

HESSONITE *v.* Garnet.

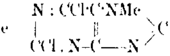
HETEROXANTHINE, *7-methylxanthine*, *7-methyl-2 : 6-dioxypurine*



$$\begin{array}{l} NH\cdot CO\cdot C\cdot NMe\diagdown \\ \vert \qquad\qquad \Vert \qquad\qquad \diagdown CH \\ CO\cdot NH\cdot C\text{——}N \end{array}$$

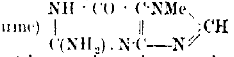
occurs together with xanthine and paraxanthine as a constituent of normal human urine (Salomon, Ber. 1885, 18, 3406; Virchow's Archiv. 1891, 125, 554); 10,000 litres yielded 22·2 grams of the mixed bases, of which 11·36 grams was heteroxanthine (Salomon and Kruger, Zeitsch. physiol. Chem. 1898, 24, 364); it occurs also with xanthine in the urine of the dog (Salomon, *ibid.* 1887, 11, 410). Heteroxanthine appears to be a product of the metabolism of theobromine and caffeine, for when rabbits, dogs, or men are dosed with these alkaloids, heteroxanthine appears in the urine (Bondzynski and Gottlieb, Ber. 1895, 28, 1113). According to Albanese (Gazz. chim. ital. 1895, 25, ii. 298) heteroxanthine is an intermediate product in the transformation that caffeine undergoes in the organism, the methyl groups being removed one by one until xanthine is obtained, and this is converted into urea and ammonia. Heteroxanthine acts as a powerful diuretic on dogs and rabbits when hypodermically injected in small doses; larger doses are toxic, an injection of 1 gram killed a dog weighing 8 kilos. in 10 days (Albanese, *l.c.*). (*Cp.* also Kruger and Salomen, Zeitsch. physiol. Chem. 1895, 21, 169; Schmiedeberg, Ber. 1901, 34, 2556.)

The synthesis of heteroxanthine from theobromine has been effected by Fischer (Ber. 1897, 30, 2400). When 2 : 6 dichloro-7-methylpurine



$$\begin{array}{l} N : CCl\cdot C\cdot NMe \\ \vert \qquad\qquad \Vert \qquad\qquad \rangle CH \\ CCl\,.\,N\text{–}C\text{——}N \end{array}$$

, obtained by the action of phosphoryl chloride on theobromine, is heated at 120°–125° with hydrochloric acid (sp.gr. 1·19), it is converted into the hydrochloride of 7-methylxanthine or heteroxanthine. Krüger and Salomon (Zeitsch. physiol. Chem. 1898, 26, 389) also obtained it by the action of nitrous acid on *epiguanine*, 7-methylguanine (2-amino-6-oxy-7-methylpurine)



$$\begin{array}{l} NH\cdot CO\cdot C\cdot NMe\diagdown \\ \vert \qquad\qquad\qquad \Vert \qquad\qquad \rangle CH\,; \\ C(NH_2)\,.\,N\cdot C\text{——}N\diagup \end{array}$$

and as Fischer (*l.c.*) has synthesised epiguanine, this method of preparation is also synthetical. Traube and Dudley (Ber. 1913, 46, 3845) obtained heteroxanthine by the action of nitrous acid on 1 : 7-dimethylguanine.

Heteroxanthine is a crystalline powder; when heated gradually it melts and decomposes at 341°–342°, when heated rapidly it darkens at 360°, and melts and decomposes at 380°. It dissolves in 142 parts of boiling water (Fischer, *l.c.*), or in 7575 parts of alcohol at 17°, or in 2250 parts at the boiling temperature (Bondzynski and Gottlieb, Ber. 1895, 28, 1113). Heteroxanthine possesses both acidic and basic properties, the basic dissociation constant k_b being 3·754K; and the acidic dissociation constant k_a being 1276K, where K is the dissociation constant of water (Wood, Chem. Soc. Trans. 1906, 1840).

Heteroxanthine forms salts with acids that are readily dissociated in water, the *hydrochloride* crystallises in tufts of transparent crystals, and yields a microcrystalline platinichloride; the *sulphate* $C_6H_6O_2N_4\cdot H_2SO_4$ is decomposed by water. Heteroxanthine forms a characteristic *sodium* derivative $NaC_6H_5O_2N_4{,}5H_2O$, crystallising in plates or prisms, melting at about 300°, readily soluble in water, sparingly so in sodium hydroxide; the *potassium* derivative has similar properties and a higher melting-point (Salomon, Ber. 1885, 18, 3406; Virchow's Archiv. 1891, 125, 554). Heteroxanthine yields a crystalline precipitate with mercuric chloride, and forms a crystalline derivative with silver nitrate. It is also precipitated by copper acetate, phosphotungstic acid or lead acetate in the presence of ammonia (Salomon, *l.c.*). It is differentiated from hypoxanthine, xanthine, and guanine by the sparing solubility of its sodium derivative in sodium hydroxide; it differs from paraxanthine in being amorphous and sparingly soluble, and in not yielding a precipitate with picric acid in the presence of hydrochloric acid.

When a solution of heteroxanthine containing chlorine water and nitric acid is evaporated, the residue develops a red colour with ammonia, becoming blue on the addition of sodium hydroxide. On oxidation with potassium permanganate in concentrated sulphuric acid heteroxanthine yields three of its four nitrogen atoms as ammonia or carbamide, and the fourth as methylamine (Jolles, Ber. 1900, 33, 2126, 2120).

By electrolytic reduction in sulphuric acid solution, heteroxanthine yields 7-methyl 2 oxy-1:6-dihydropurine (Tafel and Weinschenck, Ber. 1900, 33, 3374). M. A. W.

HETOCRESOL. Trade name for cinnamyl-*m*-cresol. Used as a dusting powder in surgery.

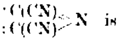
HETOFORM. Formin benzoate.

HETOL. An aqueous solution of sodium cinnamate. Used in the treatment of inoperable cancer.

HETRALIN. A resorcin hexamethylenetetramine preparation, containing 9 p.c. of formaldehyde.

HEWETTITE. A hydrated vanadate of calcium $CaO{\cdot}3V_2O_5{,}9H_2O$, crystallised in the orthorhombic system. It forms mahogany-red, earthy masses, composed of minute silky needles, and occurs somewhat abundantly as an oxidation product of patronite (*q.v.*) at Minasragra, near Cerro de Pasco in Peru. The mineral fuses readily to a dark-red liquid, and is slightly soluble in water. Sp.gr. 2·55.

Metahewettite is identical with hewettite in composition and in crystallising in the orthorhombic system, but it differs somewhat in its optical characters and behaviour during dehydration. It is found as a dark-red, powdery impregnation in sandstone at Paradox Valley in Colorado, and over a wide area in eastern Utah. L. J. S.



HEXACYANOGEN $CN{\cdot}C\begin{matrix}\nearrow N{\cdot}C(CN)\searrow \\ \searrow N{:}C(CN)\nearrow\end{matrix}N$ is obtained by heating a mixture of cyanuric tricarboxylamide and phosphoric oxide in a vacuum at 250°. Is decomposed by water with production of cyanuric acid. Is unattacked by the halogens. When strongly heated decomposes forming dicyanogen (Ott, Ber. 1919, 52 [B], 656).

HEXADECYLENEDICARBOXYLIC ACID, *Tetradecylsuccinic acid* $C_{18}H_{34}O_4$. Prepared by heating hexadecylenedibromide, potassium cyanide, and alcohol at 160°–190°, and decomposing the nitrile thus formed with alcoholic potash (Krafft and Grosjean, Ber. 1890, 2355); m.p. 121°. The anhydride melts at 89°.

HEXAHYDROXYBENZENE *v.* PHENOL AND ITS HOMOLOGUES.

HEXAL. Hexamethylenetetramine sulphosalicylate.

HEXALIT. Trade name for hexamethylenetetramine salicyl sulphonic acid.

HEXAMECOL. Hexamethylenetetramine guaiacol. Used as an external disinfectant in skin diseases.

HEXAMETHYLENETETRAMINE *v.* METHYL.

HEXAMINE. Syn. for hexamethylenetetramine (*q.v.*).

HEXANATRIN. Trade name for a combination of hexamethylenetetramine and acid sodium phosphate.

HEXANEDIONE *v.* KETONES.

HEXANITRIN. Trade name for mannitol hexanitrate.

cyclo-**HEXANONE** and **HEXENONE** *v.* KETONES.

HEXOIC ACIDS *v.* CAPROIC ACIDS.

HEXOPHAN. Oxyphenylquinoline dicarbonate.

HEXOSEPHOSPHORIC ACID *v.* FERMENTATION.

HEXOSES *v.* CARBOHYDRATES.

HIBBENITE *v.* HOPEITE.

HIDDENITE. A transparent, emerald-green variety of the mineral spodumene $LiAlSi_2O_6$ (*q.v.*), used as a gem-stone. It is found with emerald in North Carolina, and has been popularly, but erroneously, known as 'lithia-emerald.' L. J. S.

HIGHGATE RESINS *v.* RESINS.

HIIROGANE. "Hiirogane" is the name applied to a blood-red coloured metal prepared either by treatment of copper with an aqueous solution of copper sulphate and verdigris, or by heating a copper alloy with a paste containing a salt of copper, borax, and some water. *Cf.* SHAKUDO (S. Miyazawa, J. Chem. Ind. Tokyo, 1917, 20, 1102; J Soc. Chem. Ind. 1918, 37, 211*a*).

HING *v.* GUM RESINS.

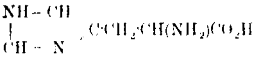
HIPPOL. Trade name for methylene-hippuric acid. Used as a urinary antiseptic.

HIPPURIC ACID, *Benzamino-acetic acid benzoylglycine* $NH(C_7H_5O)CH_2{\cdot}CO_2H$, an acid found in the urine of horses and cows and other herbivora and in human urine when benzoic acid is taken internally. It is prepared from urine by boiling with milk of lime, neutralising with HCl, concentrating to one-eighth original volume, and saturating with HCl; crude strongly coloured hippuric acid separates; it may be purified by passing chlorine into the hot aqueous solution, filtering while hot, and rapidly cooling the filtrate. May be prepared by action of benzoic anhydride on glycocoll (Curtius, Ber. 1884, 1663). Crystallises in large trimetric prisms, soluble in water, alcohol, and ethyl acetate; insoluble in light petroleum; m.p. 187·5°. Has a slightly bitter taste and reddens litmus. Decomposes on heating, forming benzonitrile and benzoic acid (Limpricht and Uslar, Annalen, 88, 133). Its aqueous solution boiled with mineral acids yields glycocoll (glycine) and benzoic acid. Oxidation with potassium permanganate in acid solution yields carbamide (Jolles, Ber. 1900, 2834). In presence of acetic anhydride, it reacts with thiocyanates forming 2-thio-3-benzoyl hydantoin, the yield being greatly influenced by the thiocyanate used: thus NH_4CNS gives 93·4 p.c., KCNS about 48 p.c. (Johnson, Hill and Bailey, J. Amer. Chem. Soc. 1915, 2406). Hippuric acid may be detected in urine by treating a few c.c. with sodium hypobromite, just sufficient being taken to decompose the carbamide and impart a permanent yellow colour to the solution. If hippuric acid is present, a characteristic orange- or brownish-red precipitate is formed on boiling the solution (Dehn, J. Amer. Chem. Soc. 1908, 1508). It may be estimated by hydrolysing the hippuric acid, extracting the benzoic acid with chloroform and titrating with sodium ethylate; this method can be used for its estimation in urine (Folin and Flanders, J. Biol. Chem. Soc. 1912, 11 Proc xxvii).

HIPTAGIN. $C_{10}H_{14}O_8N_2.\frac{1}{2}H_2O$, a glucoside, from *Hiptage Madablota* (Gaertn). Forms silky needles, m.p. 110°; $[\alpha]_D$ +3·5 in 5 p.c. acetone solution. Alkalis evolve ammonia and form hydrocyanic acid. For other reactions and probable constitution and mode of origin, *see* Gorter, Bull. Jard. bot. Buitenzorg. 1920, [iii.] 2, 187.

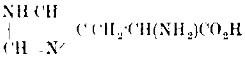
HISTAMINE. Trade name for β-Iminazolylethylamine *v.* Ergot.

HISTIDINE, *glyoxaline-4-alanine, l-α-amino β-glyoxaline-4* (or 5)-*propionic acid, β-iminazole-α-aminopropionic acid*

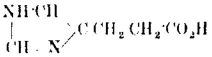


was discovered by Albrecht and Kossel (Zeitsch. physiol. Chem. 1896, 22, 176) among the hydrolytic products of the protamine sturine, which contain 12·9 p.c. histidine, 12 p.c. lysine, and 58·2 p.c. arginine (Kossel, *ibid.* 1900, 31, 207). Hedin (*ibid.* 1896, 22, 191) isolated it from the bases precipitated by silver nitrate from the decomposition products of other proteins. Kutscher (*ibid.* 1898, 25, 195) found it present in antipeptone obtained by the pancreatic digestion of fibrin. Lawroff (*ibid.* 1899, 28, 388) and Abderhalden and Rona (*ibid.* 1904, 41, 278) prepared it from thymus histon; and Koch (J. Biol. Chem. 1911, 9, 121) established its presence among the hydrolytic products of the globulin from pigs' thyroids. Jones obtained 15 grams of histidine hydrochloride from 2 litres of a concentrated suspension of red blood corpuscles (J. Biol. Chem. 1918, 33, 429). Hanke and Koessler prepared 15 grams pure histidine dihydrochloride from 500 c.c. of blood corpuscle paste (J. Biol. Chem. 1920, 43, 521) Histidine occurs also with arginine and lysine among the hydrolytic products of vegetable proteins, notably in the seeds and seedlings of *Picea excelsa* (Linn.), *Pinus sylvestris* (Linn.), *Cucubita Pepo* (Linn.), *Lupinus luteus* (Linn.), and *Pisum sativum* (Linn.); in the case of conifer seeds 300 grams of the dry proteid yield 3 grams histidine hydrochloride, 19 grams arginine nitrate, and 3 grams lysine picrate (Schulze and Winterstein, Zeitsch. physiol. Chem. 1899, 28, 459, 465; 1901, 33, 547). It is present in *secale coruntum* (Frankel, Rainer, Biochem. Zeitsch. 74, 167), in J. artichoke and salsify (Schulze and Trier, Zeitsch. physiol. Chem. 1912, 81, 53), in some of the lower fungi (Sullivan, Science, 1913, 38, 678; and Reed, J. Biol. Chem. 1914, 19, 260); *see* also Chapman, Chem. Soc. Trans. 1914, 105, 1895, for probable presence in *hops*. It is found in soils (Schreiner and Shorey, J. Biol. Chem. 1910, 8, 381; Skinner, Bied. Zentr. 1913, 42, 213, from 8th Proc. Int. Cong. Appl. Chem. 1912; Lathrop, Chem. Zentr. 1917, 11, 560), in fresh fish (Suzuki, J. Agric. Tokyo, 1912, 5, 1), and in diphtheria bacillus (Tamura, Zeitsch. physiol. Chem. 1914, 89, 295).

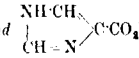
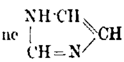
The constitution of histidine as ***α-amino-β-glyoxaline-4*** **(or 5)-*propionic acid*, has been established by the work of Fränkel, Pauly, Knoop and** Windaus, and Pyman. Fränkel (Monatsh. 1903, 24, 229) showed that histidine contains a *carboxyl* group, since it displaces carbon dioxide from silver and copper carbonates, and an *amino* group because on treatment with hypobromite or nitrous acid one nitrogen atom is removed and a hydroxyl group introduced. Fränkel, therefore, represented histidine by the partially expanded formula $NH_2{\cdot}C_5H_6N_2{\cdot}CO_2H$, and gave the name *histine* to the complex $—C_5H_6N_2—$, and *hydroxydeaminohistidine* or *hydroxyhistinecarboxylic acid* to the compound $OH{\cdot}C_5H_6N_2{\cdot}CO_2H$ obtained from histidine by the action of nitrous acid Pauly (Zeitsch. physiol. Chem. 1904, 42, 508) confirmed the presence of the carboxyl group in histidine by preparing the methyl ester, and proved that the *histine* complex $—C_5H_6N_2—$ contains an *imino*-group, because histidine yields a *dinaphthalene-β-sulphone* derivative, and forms a red dye with diazobenzenesulphonic chloride. These considerations, and the stability of the compound towards oxidising agents led Pauly to conclude that the complex *histine* contains an iminazole or glyoxaline ring, and that histidine is *α-amino-β-glyoxaline-4* (or 5)-*propionic acid*



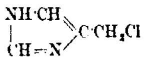
This conclusion has been confirmed by Knoop and Windaus (Beitr. Chem Physiol. Path. 1905, 7, 144), who obtained *glyoxaline-4* (or 5)-*propionic acid*



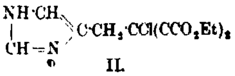
by reducing Frankel's hydroxydeaminohistidine, and showed that it is identical with the synthetic product prepared by the action of formaldehyde and ammonia on Wolff's glyoxylpropionic acid (Annalen. 1890, 260, 79). *Cf.* Frankel (Beitr. Chem. Physiol. Path. 1907, 19, 116).

Knoop (Beitr. Chem. Physiol. Path. 1907, 10, 111) also showed that by the successive oxidation of hydroxydeaminohistidine *glyoxaline-4* (or 5)-*carboxylic acid*  is obtained, which, when heated at 286°, loses carbon dioxide and yields glyoxaline 

The complete synthesis of histidine from 4 (or 5)-chloromethylglyoxaline is described by Pyman (Chem. Soc. Trans. 1911, 1386). 4 (or 5)-Chloromethylglyoxaline (I), obtained from diaminoacetone (*ibid.* 668), condenses with ethyl sodiochloromalonate to form *ethyl* 4 (or 5)-*glyoxalinemethylchloromalonate* (II)

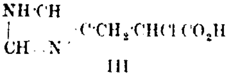


I.



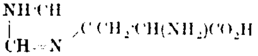
II.

This ester on hydrolysis is converted into *r-a-chloro-β-glyoxaline*-4 (or 5)-*propionic acid* (III), which reacts with ammonia to form *r-a-amino-β-glyoxaline*-4 (or 5)-*propionic acid* (IV), that is *r*-histidine



$$\begin{array}{l} NH\cdot CH \\ | \qquad\qquad >C\cdot CH_2\cdot CHCl\cdot CO_2H \\ CH=N \end{array}$$

III

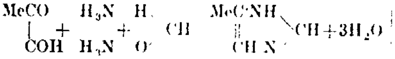


$$\begin{array}{l} NH\cdot CH \\ | \qquad\qquad >C\cdot CH_2\cdot CH(NH_2)CO_2H \\ CH=N \end{array}$$

IV.

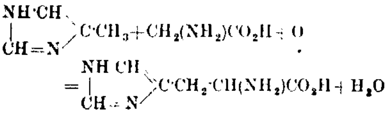
Pyman (Chem. Soc. Trans. 1916, 109, 186) also synthesised *r*-histidine from benzoyl *r*-histidine by boiling this for four hours with 20 p.c. aqueous hydrochloric acid. *r*-Histidine can be resolved by the fractional crystallisation of the salts it forms with *d*-tartaric acid into the *d*- and *l*-isomerides, and the *l*-histidine thus obtained is identical with the naturally occurring compound. *d-l*-histidine is partly resolved by means of yeast, the *d*- isomeride remaining unattacked (Abderhalden and Weil, Zeitsch. physiol. Chem. 1912, 77, 435; Ehrlich, Biochem. Zeitsch. 63, 379).

A possible explanation of the formation of histidine in the plant economy is afforded by the work of Knoop and Windaus (Beitr. Chem. Physiol. Path. 1905, 6, 292; Ber. 1906, 39, 3886; 1907, 40, 799) on the synthetic formation of iminazole derivatives from sugars and ammonia. These authors find that when a solution of glucose containing zinc hydroxide dissolved in ammonia is exposed to the sunlight at the ordinary temperature for some weeks, it is converted to the extent of 10 p.c. into 4- or 5-*methyliminazole*. It is probable that glyoxal and formaldehyde are produced as intermediate products and then react with the ammonia according to the equation



$$\begin{array}{l} MeCO \\ | \\ COH \end{array} + \begin{array}{l} H_3N \\ \\ H_3N \end{array} + \begin{array}{l} H \\ \quad >CH \\ O \end{array} = \begin{array}{l} MeC\cdot NH \\ \| \qquad\quad >CH \\ CH\cdot N \end{array} + 3H_2O$$

d-Mannose, *d*-fructose, *d*-sorbose, *l*-arabinose, or *l*-xylose also yield methyliminazole when similarly treated. The authors suggest that histidine may be formed naturally by the condensation of methyliminazole with glycocoll and simultaneous oxidation



$$\begin{array}{l} NH\cdot CH \\ | \qquad\quad >C\cdot CH_3 \\ CH=N \end{array} + CH_2(NH_2)CO_2H + O = \begin{array}{l} NH\cdot CH \\ | \qquad\quad >C\cdot CH_2\cdot CH(NH_2)CO_2H \\ CH=N \end{array} + H_2O$$

Histidine crystallises from water in needles or tables, m.p. 287° (corr.); the aqueous solution has a sweet taste (Frankel, Monatsh. 1903, 24, 229; Pyman, Chem. Soc. Trans. 1911, 1397), is feebly alkaline (Hedin, Zeitsch. physiol. Chem. 1896, 22, 191), and is optically active $[\alpha]_D -39{\cdot}74°$ (Kossel and Kutscher, *ibid.* 28, 382); $[\alpha]_D -36{\cdot}7°$ (Pyman, *l.c.*); it racemises on heating under pressure (Abderhalden and Weil, *l.c.*).

r-Histidine crystallises in quadrilateral plates, and decomposes at 283° (corr.); *d-histidine* crystallises in monoclinic plates forming elongated hexagons; it decomposes at 287°–288° (corr.), and has $[\alpha]_D +39{\cdot}3°$ (Pyman, *l.c.*, and 1916, 109, 197).

When histidine is administered as a food, or by intravenous injection very little (0·4 gram out of 10 grams) is recoverable as such in the urine; the urea and ammonia in the urine are largely increased, but the increase of allantoin is very slight. Pure *d*-histidine was obtained from the urine of rabbits fed on *d-l*-histidine (Abderhalden, Embeck, and Schmid, Zeitsch. physiol. Chem. 1909, 62, 322; 1910, 68, 395; Kowalewsky, Biochem. Zeitsch. 1909, 23, 1; Abderhalden, *ibid.* 1910, 68, 395, and *ibid.* 1911, 74, 481; Abderhalden and Weil, *ibid.* 1912, 77, 435).

For the catabolism of histidine in the animal organism, *see* Dakin and Wakeman (J. Biol. Chem. 1912, 10, 499), and, as forerunner of purine bodies in animal metabolism, Ackroyd and Hopkins (Bio-Chem. J. 1916, 10, 551).

Salts. *l*-Histidine forms stable salts with acids and their solutions are dextrorotatory.

Monohydrochloride $C_6H_9O_2N_3\cdot HCl,H_2O$ forms large colourless rhombic crystals

$$a : b : c \quad 0{\cdot}7965 : 1 : 1{\cdot}71104$$

has $[\alpha]_D +1{\cdot}74°$, m.p. 80°, and loses H_2O at 140 (Albrecht and Kossel, Zeitsch. physiol. Chem. 1896, 22, 176; Hedin, *ibid.* 191; Kossel and Kutscher, *ibid.* 1899, 28, 382; Fränkel, Monatsh. 1903, 24, 229); the *di-hydrochloride* $C_6H_9O_2N_3\cdot 2HCl$ is isomorphous with the mono-compound [$a : b : c$ 0·76537 : 1 : 1·77516], it has $[\alpha]_D +5{\cdot}3$ to 6·4° (Kossel and Kutscher, *l.c.*; Schwartze, Zeitsch. physiol. Chem. 1900, 29, 493). *Histidine cadmium chloride*

$$C_6H_9O_2N_3\cdot HCl,CdCl_2$$

melts and decomposes at 270°–275° (Schenck, *ibid.* 1904, 43, 72). Histidine gives a complex copper salt $Cu(C_6H_8O_2N_3)_2$ (Kober and Sugiura, J. Biol. Chem. 1912–13, 13, 5), and a compound with iron $(C_6H_8O_2N_3)_2Fe$ (D.R.P. 266522). *Histidine phosphotungstate*

$$(C_6H_9N_3O_2)_3,2H_3PO_4+24WO_3$$

crystallises without water of crystallisation (Wechsler, Zeitsch. physiol. Chem. 1911, 73, 140). *Histidine monopicrolonate*

$$C_6H_9O_2N_3\cdot C_{10}H_8O_5N_4$$

is yellow. The *dipicrolonate*

$$C_6H_9O_2N_3\cdot 2C_{10}H_8O_5N_4$$

is orange (Steudel, Zeitsch. physiol. Chem. 1905, 44, 157; Brigl, *ibid.* 1910, 64, 337); the *dipicrate* $C_{18}H_{15}O_{16}N_9,2H_2O$ has m.p. 86° (corr.), (Pyman, Trans. Chem. Soc. 1911, 343); the pentahydrate $C_6H_9O_2N_3(C_6H_3O_7N_3)_2,5H_2O$ has m.p. 80° (Hugouenq and Florence, Bull. Soc. Chem. Biol. 1919, 1, 102).

l-Histidine-d-hydrogen tartrate

$$C_6H_9O_2N_3,C_4H_6O_6$$

is easily soluble in water, crystallises in large well-defined prisms, and decomposes at 172°–173° (corr.); and has $[\alpha]_D +16{\cdot}3°$. *l-Histidine-l-hydrogen tartrate* is sparingly soluble in cold water, crystallises in clusters of prisms and decomposes at 234° (corr.), and has $[\alpha]_D -12{\cdot}1°$ (Pyman, *ibid.* 1397, 1400).

d-Histidine-d-hydrogen tartrate is sparingly soluble, decomposes at 234° (corr.), and has $[\alpha]_D +13{\cdot}3°$ (Pyman, *l.c.*).

r-Histidine mono-hydrochloride

$$C_6H_9O_2N_3\cdot HCl,2H_2O$$

has m.p. 117°–119° (corr.); *sesquihydrochloride*

$$(C_6H_9O_2N_3)_2·3HCl,H_2O$$

has m.p. 168°–170° (corr.); the ***dihydrochloride*** has m.p. 235°–236° (corr.); ***r-histidine mono-picrate*** $C_{12}H_{12}O_9N_6,H_2O$ decomposes at 180°–181° (corr.); the *dipicrate* $C_{18}H_{15}O_{16}N_9,2H_2O$ decomposes at 190° (corr.). (Pyman, *ibid.* 339; *cf.* Pyman, *ibid.* 1916, 109, 196).

Derivatives. *Histidine methyl ester hydrochloride* $C_5H_8N_3·CO_2Me·2HCl$ forms flat rhombic prisms, m.p. 196° (decomp.), the free ester is an oil (Pauly, Zeitsch. physiol. Chem. 1904, 42, 508). *Chlorohistidinecarboxylic acid* (*α-chloro-β-glyoxaline-4* (or 5) *propionic acid*) forms thick prisms, m.p. 191° (decomp.), the corresponding *racemic* compound decomposes at 201° (corr.) (Pyman, *ibid.* 1394), the *oxalate* of the *ester* has m.p. 161° (Windaus and Vogt, Beitr. chem. Physiol. Path. 1908, 11, 406). *Histidine anhydride* $C_{12}H_{14}O_2N_6$ forms glittering prisms, m.p. 340° (Fischer and Suzuki, Sitzungsber. K. Akad. Wiss. Berlin, 1904, 1333); the *l*-anhydride has m.p. 328° in a closed evacuated tube, crystallises with $2\frac{1}{2}H_2O$, and has $[\alpha]_D^{20}$ 66·24° in normal hydrochloric acid solution; the *dl-anhydride* also has m.p. 328°, and is obtained by heating the ethyl ester of histidine at 160° (Pauly, Zeitsch. physiol. Chem. 1910, 64, 75); the *picrate* decomposes at 255° (corr.); the *hydrochloride* at 320°. The *tetraiodo* derivative has m.p. 240°, and is amphoteric and forms a *silver salt* (Pauly, Ber. 1910, 43, 2243). *Histidylhistidine* $C_{12}H_{16}O_3N_6$ forms a yellow *picrate*, m.p. 165°–175° (Fischer and Suzuki, *l.c.*).

Alkyl derivatives. The direct methylation of histidine affects the glyoxaline ring. Under certain conditions *pentamethylhistidine* may be obtained which forms a stable chloride and a sparingly soluble aurichloride, $C_{11}H_{21}O_2N_3Au_2Cl_8$, m.p. 220°, but which does not respond to the diazo reaction (Engeland and Kutscher, Chem. Zentr. 1913, I, 28).

Trimethyl histidine occurs in fungi (Winterstein and Reuter, Zeitsch. physiol. Chem. 1913, 86, 234), it has been isolated as the aurichloride $C_9H_{17}O_2N_3Au_2Cl_8$, m.p. 183° (decomp.) (Engeland, Kutscher, Chem. Zentr. 1913, I, 28, from Zentr. physiol. 1912, 26, 569). Barger and Ewins (Bio-Chem. J. 1913, 7, 204) prove the identity of that obtained from various sources. The *mono-picrate* has m.p. 201°–202°, the *dipicrate*, m.p. 213°. Trimethyl histidine has $[\alpha]_D+46·5°$.

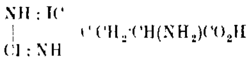
Acyl derivatives. Of the *acyl* derivatives of histidine the *benzoyl* has m.p. 249° (decomp.) (Pauly, *l.c.*; Frankel, *l.c.*); *benzoyl-r-histidine*, $C_{13}H_{13}O_3N_3$ (from *α-benzoylamino-β-glyoxaline-4* (or 5) *acrylic acid* on reduction with sodium amalgam in aqueous suspension), has m.p. 248° (corr. decomp.); it crystallises in hard, glistening prisms with one molecule of water of crystallisation, which is lost at 115°. The *hydrochloride* crystallises from water in hard glistening prisms, m.p. 232° (corr. efferv.). The *picrate* crystallises in bunches of yellow feathery needles, m.p. 226° (corr.) (Pyman, Chem. Soc. Trans. 1916, 109, 195). Benzoylation of histidine methyl ester yields a tribenzoyl derivative

$$CH·NH(C_6H_5CO):C(NHC_6H_5CO)·$$
$$CH_2·CH(NHC_6H_5CO)CO_2Me$$

m.p. 219° (not sharp), which does not give the red colour with diazobenzene sulphonate; on heating the glyoxaline closes again and the product gives the characteristic colour reaction (Kossel and Edlbacher, Zeitsch. physiol. Chem. 1915, 93, 396; *cf.* Inouye, *ibid.* 1913, 83, 79, who points out that in order to obtain the colour reaction excess of benzoyl chloride must not be present). The *dinaphthalene β-sulphone* $C_6H_7O_2N_3(SO_2·C_{10}H_7)_2$ melts at 149°–150° (Pauly); *p-Nitrobenzoylhistidine*

$$C_6H_8N_3O_2·CO·C_6H_4·NO_2$$

m.p. 251°–252° (Pauly). *Benzoyldiiodohistidine*, m.p. 161°–164°, in an evacuated tube; and *p-nitrobenzoyldiiodohistidine*, m.p. 172° (decomp.) are derivatives of the unknown diiodohistidine



$$\begin{array}{l}NH:IC\\ \quad|\qquad\qquad C·CH_2·CH(NH_2)CO_2H\\ CI:NH\end{array}$$

they give orange-red colorations with diazobenzenesulphonic acid and sodium carbonate, and form silver salts (Pauly, Ber. 1910, 43, 2243). *d-α-Bromoisohexoyl-l-histidine methyl ester*

$$C_4H_9·CHBr·CO·NH·CH(C_4H_5N_2)CO_2Me$$

has m.p. 175° (corr.); *d-α-bromoisohexoyl-l-histidine* $C_{12}H_{18}O_3N_3Br$ has m.p. 118° (corr.); *l-leucyl-l-histidine*

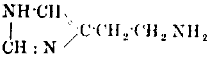
$$C_4H_9·CH(NH_2)·CO·NH·CH(C_4H_5N_2)CO_2H$$

crystallises in plates or prisms, containing H_2O, which it loses at 100°/15–20 mm., and has m.p. 178° (corr.) (decomp.), the *copper* salt forms deep violet crystals; *formyl-l-histidine* has m.p. 203° (corr.) (Fischer and Cone, Annalen, 1908, 363, 107).

Colour reactions. Histidine gives the *biuret* reaction (Herzog, Zeitsch. physiol. Chem. 1903, 37, 248). It also gives the Weidel pyrimidine reaction under the following conditions: a solution of histidine hydrochloride and a little potassium chlorate is evaporated to dryness, hydrochloric acid containing one drop of nitric acid added and the solution again evaporated; on exposing the residue to ammonia fumes an intense red colour is produced, becoming reddish-violet on the addition of sodium hydroxide (Frankel, *l.c.*). With diazobenzenesulphonic chloride in the presence of sodium carbonate histidine gives a dark cherry-red coloration, becoming orange on the addition of an acid. This is an extremely delicate test for histidine, and with the exception of tyrosine no other product of protein hydrolysis gives a similar reaction (Pauly, Zeitsch. physiol. Chem. 1904, 42, 508, and *ibid.* 1915, 94, 427; *cf.* Inouye, *ibid.* 1913, 83, 79, who applies the test for histidine in presence of tyrosine after addition of benzoylchloride, and Totani, Bio-Chem. J. 1915, 9, 385, who reduces the coloured solution obtained by Pauly's reaction (by means of zinc dust in presence of hydrochloric acid) and then makes it strongly alkaline with ammonia: if the original solution contained histidine it will now become a bright golden yellow). Histidine develops a yellow colour with bromine water; this disappears on warming, but after a time a pink colour appears, which afterwards deepens to a wine-red. The reaction is sensitive with solutions of 1 : 1000, but is destroyed by too large excess of bromine water (Knoop, Beitr. Chem. Physiol. Path. 1908, 11, 356).

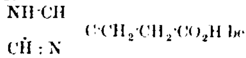
A method for estimating histidine colourimetrically is based upon the Pauly diazo-reaction (Weiss, Sobolev, Biochem. Zeitsch. 1913, 58, 119): a mixture of sulphanilic acid in hydrochloric acid and sodium nitrite are added to the solution to be investigated, and then 10 p.c. sodium carbonate added. The total volume is kept constant, and the colour obtained compared with that given (under similar conditions) by a 1/10,000 histidine solution. The histidine can also be estimated volumetrically by titrating the stable histidine dye with titanium trichloride (Lautenschlager, Zeitsch. physiol. Chem. 1918, 102, 226). For the estimation of histidine in proteins by hydrolysis followed by bromination, *see* Thrum and Trowbridge (J. Biol. Chem. 1918, 34, 343). For a microchemical method, *see* Kober and Suguira, J. Amer. Chem. Soc. 1913, 35, 1546, and Van Slyke, J. Biol. Chem. 1911, 9, 185; *ibid.* 1911-12, 10, 29; *ibid.* 1912, 12, 279; *ibid.* 1915, 23, 411. For the phosphotungstate precipitate of histidine, *see* Wechsler, Zeitsch. physiol. Chem. 1911, 73, 141.

Decomposition. When histidine undergoes anærobic bacterial cleavage by the action of putrefying pancreas, it is converted almost quantitatively by the loss of carbon dioxide into 4 (or 5)-*β-aminoethylglyoxaline* (*β-iminazolylethylamine*)



$$\left.\begin{array}{l}\mathrm{NH{\cdot}CH}\\ \mid\\ \mathrm{CH:N}\end{array}\right\rangle\mathrm{C{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2}$$

; *iminazolylpropionic acid*



$$\begin{array}{l}\mathrm{NH{\cdot}CH}\\ \qquad\qquad\mathrm{C{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H}\\ \mathrm{CH:N}\end{array}$$

being the other product (*v.* Ackermann, Zeitsch. physiol. Chem. 1910, 65, 504). The 4 (or 5)-β-aminoethylglyoxaline thus obtained is identical with the base prepared synthetically by Windaus and Vogt (Ber. 1907, 40, 3691) from ethyl iminazolylpropionate; or by Pyman (Chem. Soc. Trans. 1911, 668) from diaminoacetone, and is also identical with one of the *ergot* bases isolated by Barger and Dale (Phil. Trans. 1910, 2592), and which is also present in Popielski's *vasodilatin* (Barger and Dale, J. Physiol. 1911, 41, 499); *see* Mellanby and Trout, who isolated a bacillus which splits off carbon dioxide from histidine and converts it to β-iminazolylethylamine; also Raistrick (Bio-Chem. J. 1917, 11, 71; *ibid.* 1919, 13, 446), who found that bacteria of the *Coli*-typhus group convert histidine into urocanic acid (β-iminazolylacrylic acid in certain media. *l*-Histidine is converted to the extent of 11 p.c. -*l* into *d*-β-iminazoylactic acid by the prolonged action of *Proteus vulgaris* in a protein-free nutrient media (Hirai, Act. Schol. Med. Kyoto. 1919, 3, 49). *Bacillus coli communis* transforms histidine into histamine to the extent of 50 p.c. in the presence of glycerol or dextrose and potassium nitrate or ammonium chloride (Koessler and Hanke, J. Biol. Chem. 1919, 39, 539; 1920, 43, 529, 543). It has a direct stimulating action on plain muscle; cardiac muscle is mildly stimulated, and skeletal muscle is not affected. The drug produces narcosis, and is a mild stimulant to the salivary glands and pancreas; for its toxic effect, *cf.* Freund (Chem. Zentr. 1914, 1, 1200 from Zeitsch. offentl. Chem. 20, 61). M. A. W.

HOANG-NAN *v.* NUX VOMICA.

HOFMANN'S VIOLET *v.* TRIPHENYLMETHANE COLOURING MATTERS.

HOG GUM *v.* GUMS.

HOLARRHENINE. $C_{24}H_{38}ON_2$ an alkaloid discovered by Pyman, in 1913, in the bark of *Holarrhena congolensis* (Stapf.), silky needles, m.p. 197°–198° (corr.). Insoluble in water, readily soluble in alcohol or chloroform but sparingly so in cold ethyl acetate, acetone, or ether. $[\alpha]_D$ 7·1° in chloroform. The ***hydrobromide*** $C_{24}H_{38}ON_2,2HBr,3H_2O$ crystallises from water in flat needles, m.p. 265°–268° (corr.), after drying. Readily soluble in hot, sparingly so in cold, water; $[\alpha]_D + 12{\cdot}1°$ for the anhydrous salt.

Acetylholarrhenine prepared by the action of acetic anhydride and anhydrous sodium acetate on holarrhenine crystallises from acetone in large colourless oblong plates, m.p. 180° (corr.). Insoluble in water, sparingly soluble in cold alcohol, acetone, or ether, readily soluble in chloroform (Pyman, Chem. Soc. Trans. 1919, 163).

HOLLANDITE. A manganese ore of essentially the same composition as psilomelane, but occurring in a crystallised condition, usually as fibrous masses and sometimes as tetragonal crystals. It is a manganate with the general formula $mR_2''MnO_5 + nR_4'''(MnO_5)_3$, where R″ is Mn, Ba, K_2, H_2, (Fe, Ca, Mg, Na, Co, Ni, Cu), and R‴ is Mn, Fe, (Al). The extreme values shown in four analyses are: MnO_2 65·63–75·05, MnO 5·12–14·20, Fe_2O_3 4·43–10·56, BaO 2·96–17·59, K_2O 0–3·31, H_2O 0–1·10 p.c. The colour is greyish-black, and the lustre submetallic; sp.gr. 4·70–4·95; H. 4–6. The mineral occurs abundantly in the manganese ore deposits at several places in Central India, and is largely exported from the mines at Sitapár and Bálághát. Closely allied minerals, perhaps identical with hollandite, are the crystalline manganates romanechite (containing less iron and more water) from Romanèche, France, and coronadite (with high lead and low barium) from Arizona. (L. L. Fermor, The Manganese Ore Deposits of India, Mem. Geol. Survey India, 1909, 37; Rec. Geol. Survey India, 1917, 48, 103.) L. J. S.

HOLMIUM. Ho. At. wt. 163·4. An element discovered by Cleve in the terbia of Mosander or erbia of Berlin, giving a pale yellow oxide and yellow salts with a slight tinge of orange (Holmberg, Arkiv. Kem. Min. Geol. 1911, 4, No. 2 and No. 10).

According to Forsling (Bihang K. Svenska Vet. Akad. Handl. 1902–1903, 28, ii. No. 1) holmium is not an individual substance but a mixture of several components to which correspond the different absorption bands. It probably consists of dysprosium with its two components as well as of at least four other substances. Langlet (Arkiv. Kem. Min. Geol. 1907, 2, No. 32), however, was unable to find any evidence of a decomposition of holmia into several components, and the later observations of Holmberg appear to have established the individuality of the element. For observations on the relative advantages of phthalic acid and sodium nitrite in separating holmium from yttrium, *see* Yntema and Hopkins (J. Amer. Chem. Soc. 1918, 40, 1163).

HOLOCAINE *v.* SYNTHETIC DRUGS.

HOMATROPINE *v.* TROPEINES.

HOMBERG'S PHOSPHORUS *v.* CALCIUM.

HOMOANTHRANILIC ACID *v.* AMINO ACIDS (AROMATIC).

HOMOCATECHOL *v.* *Homopyrocatechol,* PHENOL AND ITS HOMOLOGUES.

HOMOGENTISIC ACID *v.* PHENYLACETIC ACID.

HOMOPILOPIC ACID *v.* JABORANDI.

HOMORENON *v.* ADRENALINE; SYNTHETIC DRUGS.

HOMOTERPENYLIC ACID *v.* LACTONES.

HONE *v.* WHETSTONE.

HONEY. Honey is the substance secreted by the working-bee (*Apis mellifica*) from the nectar of flowers, and deposited by the insect in the wax-cells forming the honeycomb. Its essential constituents are varying quantities of the sugars, dextrose, lævulose, and sometimes cane-sugar, together with a small quantity of water. It also contains very small quantities of wax, colouring matters, aromatic substances, phosphoric acid, nitrogenous compounds, and occasionally mannitol.

Lactase, proteases and lipases are not present in honey and the occurrence of inulase is doubtful. Invertase is present more in natural honey than in that produced by bees fed on sugar. This enzyme is destroyed when honey is heated to 60°. The presence of invertase in honey explains why the cane sugar in honey gradually disappears when the honey is kept for some considerable time. Honey also contains catalase and diastase, and an estimation of the activity of the diastase is an indication of the genuineness of the honey. According to Hudson and Sherwood (J. Amer. Chem. Soc. 1920, 42, 116), American honey-dew honey occasionally contains considerable quantities of melecitose.

The relative proportions in which the above-named sugars occur is very variable. Thus Hehner (Analyst, 9, 164) obtained the following results from the analysis of 25 different varieties:

	Maximum	Minimum	Mean
Water . .	23·26	12·43	19·3
Glucose . .	75·34	61·42	67·2
Other constituents	16·51	8·48	13·5

In 8 cases the amount of glucose was unaltered by inversion, in 7 increased, and in the remainder slightly diminished.

Sieben (Bied. Zentr. 1885, 134) analysed 60 specimens of honey, and states that the quantity of cane-sugar may amount to as much as 4 or even 8 p.c., and that the ratio of dextrose to lævulose varies considerably, the total amount of these two sugars being 68-78 p.c. The average composition of the 60 specimens was as follows:

Dextrose . . .	34·71 p.c.
Lævulose . .	39·24 ,,
Sucrose	1·08 ,,
Water	19·98 ,,
Non-saccharine matter .	5·02 ,,

For the composition of Russian honey *see* Sarin, Zeitsch. Untersuch. Nahr. Genuss. 1913, 25, 131; Analyst, 1913, 149.

Turning now from average results to the composition of the several varieties, we find the following table of the analysis of 9 specimens of honey from different localities (J. C. Brown, Analyst, 1878, 257).

	England	Wales	Normandy	Germany	Greece	Lisbon	Jamaica	California	Mexico
Water expelled at 100° .	19·10	16·40	15·50	19·11	19·80	18·80	19·46	17·90	18·47
Water expelled at a high temperature and loss .	7·60	6·56	4·95	11·00	7·80	6·66	7·58	8·13	10·03
Lævulose . . .	36·60	37·20	36·88	33·14	40·00	37·26	33·19	37·85	35·96
Dextrose . . .	36·55	39·70	42·50	36·58	32·20	34·94	35·21	36·01	35·47
Sucrose . . .					—	1·20	2·20	—	?
Wax, pollen, and insoluble matter . .	trace	trace	trace	trace	0·05	1·00	2·10	trace	trace
Mineral matter . .	0·15	0·14	0·17	0·17	0·15	0·14	0·26	0·11	0·07

For a large number of other analyses *see* Fiehe and Stegmuller (Arbeit. Kaiserl. Gesund. 1913, 44, 78; Analyst, 1913, 265).

The characteristic composition of ordinary honey can be judged from the analysis of 10 samples of genuine honey by Hoitsema (Zeitsch. anal. Chem. 1899, 439) which gave the following results:—

Specific gravity . .	1·102–1·140
Water . . .	8·3–17·8 p.c.
Rotation . .	– 9·1° to –3·0°
Ash	0·12–0·34 p.c.
Pollen and wax . .	0·02–0·46 ,,
Reducing sugars . .	71·2–74·4 ,,
Sucrose . . .	0·2–6·4 ,,

The amount of water present in honey varies with the dryness of the season and the conditions of storage, evaporation being much lessened when all the cells of the comb are closed (Graftian, Analyst, 1895, 251).

Erlenmeyer and v. Plata (Rep. Pharm. 23, 610) found that in 6 samples of good honey the amount of water varied from 17·5 to 19·5 p.c., whilst a liquid honey from Senegal contained as much as 25·6 p.c. The amount of phosphoric acid present (calculated on the dried substance) varied from 0·0123 to 0·883 p.c.

Sumatra honey, formed by *Apis indica*, contains water, dextrose, lævulose, a little wax and pollen, and 0·23 p.c. ash, but no cane-sugar or dextrin (Franchimont, Rec. trav. chim. 1, 223). An Ethiopian honey, made in hollows without wax by a kind of mosquito, gave the following result on analysis (Compt. rend. 88, 292):—

Water	25·5
Lævulose and dextrose (⅛) .	32·0
Mannitol	3·0
Dextrin	27·9
Ash	2·5
Other constituents . . .	9·1

It has also been shown that honey frequently but not invariably contains a small quantity of formic acid. It amounts only to from 0·0060 to 0·0100 p.c., therefore most of the acidity of honey must be due to some other acid, possibly malic acid (Farnsteiner, Zeitsch. Nahr. Genussm. 1908, 15, 598; Fincke, *ibid.* 1912, 23, 255).

The formic acid may be estimated by conversion into sodium formate, heating with conc. sulphuric acid, and measuring the volume of carbon monoxide evolved. As lactic acid also gives this gas it must be oxidised with potassium permanganate and estimated as oxalate and a correction applied (Merl, Zeitsch. Nahr. Genussm. 1908, 16, 385; Heiduschka and Kaufmann, *ibid.* 1911, 21, 375; Heiduschka, Chem. Zeit. 1911, 35, 1104).

If bees be fed on dextrose only, the honey formed contains that sugar alone. Heather-fed honey, on the other hand, contains invert sugar only, whilst Cuban honey contains dextrose in larger quantity than lævulose (Röders, Chem. Zentr. 1864, 1002).

Eucalyptus honey is produced in Australia by a black bee which builds large hives on the *Eucalypti* containing as much as 5000 kilogs. of honey. The honey is a thick syrup, having a strong aromatic odour (Maquenne, Ann. Chim. [vi.] 17, 495).

Marck has given the following figures for the composition of East Indian honeys (Analyst, 1890, 196):—

Glucose, about 30 p.c.; lævulose, 23–37 p.c.; ash, 0·12–0·54 p.c.; sp.gr. 1·3099–1·3586; rotation +13° to 2° 54′.

In the honey of *Polybia apicipennis* large crystals of cane-sugar are frequently found (J. pr. Chem. [ii.] 71, 314). The honey of the Mexican honey-ant is almost a pure solution of lævulose, and when dried *in vacuô*, has the composition $C_6H_{12}O_6,H_2O$. It contains traces of a volatile acid which reduces silver salts (J. pr. Chem. [ii.] 58, 430).

To obtain honey the syrup is first simply allowed to flow from the comb at the ordinary temperature, the portion thus collected being known as 'virgin-honey.' As soon as the flow ceases, the residual comb is heated and pressed, by which means a darker and less pure variety is obtained. According to Zwilling (Bied. Zentr. 1885, 67) it is best to gather the honey when it has thickened and the cells are sealed, as then sufficient sugar and formic acid are present.

The honey-syrup remains clear for a long time if kept in the dark, but on exposure to light dextrose gradually separates, and such varieties as contain that sugar in the largest quantity become sufficiently solid to be cut with a knife into pieces which are not hygroscopic. As, however, the composition of honey is so variable, the consistency and colour likewise differ considerably in the different samples. Thus Narbonne honey has a light yellow colour, and forms an almost solid mass, whereas Cuban honey is a clear and almost colourless syrup.

Honey has a sp.gr. of from 1·439 to 1·448. When diluted with water it gives a somewhat cloudy, faintly acid solution, the cloudiness being due to small quantities of proteid matter. Its specific rotatory power varies from −5·5 to +2, but dextrorotatory honey is exceptional.

Frühling has shown (Zeitsch. öffentl. Chem. 4, 410) that freshly prepared solutions of honey in cold water show an abnormal rotation, which, after some hours, becomes normal. This behaviour, which is due to 'bi-rotation,' may lead to erroneous observations unless care is taken to dissolve the honey in boiling water and to add about 0·1 p.c. of ammonia.

A pure solution of honey does not readily undergo alteration in the air, but when impure, both acid and alcoholic fermentation speedily take place. An alcoholic liquor known as 'mead' (Ger. *Meth*; Fr. *Hydromel*) has long been prepared from honey by fermentation. The process is, however, frequently unsuccessful, owing to the fact that honey does not usually contain sufficient nitrogenous food for the sustenance of the ferment. If a suitable food be added, the fermentation proceeds smoothly and with certainty (Gastine, Compt. rend. 109, 479). According to Boussingault (Ann. Chim. [iv.] 26, 362) the quantity of carbon dioxide formed during fermentation is greater, and the quantity of alcohol less, than would be expected from the amount of sugar fermented. Thus, instead of the calculated quantities of 193·6 parts of alcohol and 170 parts of carbon dioxide, he obtained 177·6 parts of alcohol, and 190 parts of carbon dioxide.

For medicinal purposes honey is purified by warming on the water-bath, and straining it through flannel which has been previously moistened with hot water. The purified compound is known as *Mel depuratum*. Dietrich (Chem. Zentr. 1877, 318) brought a filtered solution of 1 part of honey in 3 parts of water on to a dialyser, and found that 50 p.c. of the honey passed through. The solution of the crystalloids gave on evaporation a honey having an unusually pleasant aromatic taste. The colloidal liquid, in which gummy floccule remained suspended, gave on evaporation a syrup possessing a purely sweet, insipid, non-aromatic taste.

In order to purify honey Riecker (J. 1873, 1066) adds a little precipitated aluminium hydroxide, which carries down any foreign substances present. If ordinary honey be shaken with absolute alcohol, dextrose remains behind. Ether precipitates lævulose from the alcoholic solution, and the ethereal solution when shaken with lime loses tannic acid, whilst wax remains in solution.

Honey is frequently adulterated with starch-sugar, invert-sugar, molasses, water, &c., and owing to the wide variations in the composition of genuine honey such adulteration is frequently difficult to detect (Racine, Zeitsch. öffentl. Chem. 1902, 281).

For a method of detecting commercial invert sugar in honey by means of β-naphthol which gives a Bordeaux red to bluish-violet colour with an ethereal extract of adulterated honey, *see* Litterschied, J. Soc. Chem. Ind. 1913, 376.

Dextrorotatory honey was formerly regarded with suspicion (Haenle, Zeitsch. anal. Chem. 1894, 99), but it has been shown that pine-honey, and honey made by bees using honey-dew, contain a dextrin which can be isolated by precipitation with alcohol, and is strongly dextrorotatory (König and Karsch, Zeitsch. anal. Chem.

1895, 1; Raumer, *ibid.* 1896, 397; Hilger, Zeitsch. Nahr. Genussm. 1904, 189). For a detailed account of the 'honey-dextrins' of pine-honey, *see* Haenle and Scholz (Zeitsch. Nahr. Genussm. 1903, 1027)

Several methods have been recommended for distinguishing between genuine and adulterated honey. Brautigam states that genuine honey contains an albumin by the reactions of which it can be distinguished (Pharm. Zeit. 47, 109). Methods for the microscopic examination of honey have been described by Dietrich (Analyst, 1896, 255). Langer has found in natural honey an inverting ferment which can be precipitated by alcohol and tested on cane-sugar (Zeitsch. angew. Chem. 1902, 1041). For the biological examination of honey as a test of its genuineness, *see* Gadamer and Laske, Arch. Pharm. 1916, 254, 306

Adulteration with starch syrup, which usually contains erythro-dextrin and amylo-dextrin can usually be detected by adding methyl alcohol to the conc. aqueous solution, when the dextrins are precipitated. The addition of molasses is best detected by testing for raffinose with basic lead acetate (Beckmann, Zeitsch. anal. Chem. 1896, 263).

Ley's reagent, an ammoniacal solution of silver oxide, when warmed with a strong solution of pure honey gives a greenish coloration, but if the honey is adulterated the liquid becomes dark brown or black (Utz, Zeitsch. angew. Chem. 1907, 993).

If 1 gram of honey be rubbed down with ether in a mortar, the ether filtered off and evaporated, and the residue treated with a drop of a solution of 1 gram resorcinol in 100 c.c. of hydrochloric acid of sp.gr. 1·19, only a momentary pink colour will be obtained with pure honey, whilst adulterated or artificial honey will give an orange-red colour, changing through cherry-red to a strong brown-red (Fiehe, Zeitsch. Nahr. Genussm. 1908, 75; Keiser, Analyst, 1909, 299; *cf.* Halphen, Ann. Falsif. 1912, 5, 105; Stacklin, *ibid.* 1912, 5, 116; Fiehe and Stegmüller, Arbb. Kais. Gesundh-Amt. 1912, 40, 305; J. Soc. Chem. Ind. 1912, 31, 943; Analyst, 1912, 449).

Adulteration with cane-sugar may be detected by determining the reducing power of the honey with Barreswil's solution, both before and after inversion. This is not very reliable, as in cases where the bees feed on sucrose it is found in the honey, though the larger proportion undergoes inversion in the insect's stomach (Raumer, Zeitsch. anal. Chem. 1902, 333; *see* also Lipmann, Analyst, 1889, 20; Bakker, Rec. Trav. Chem. 1921, 40, 600).

Sugar in honey is estimated by diluting with twice its volume of water, and ascertaining the sp.gr. This varies between 1·101 and 1·115. The first number corresponds to 24 p.c., and the latter to 27 p.c. of sugar in the solutions, or to 72 p.c. and 82 p.c. in the original honey (Flückiger, Pharmaceut. Chemie, [ii.] 267).

Wiley has described a process for the estimation of lævulose in honey, &c., based on the fact that its optical rotation is much diminished with rise of temperature. The observation tube of the polarimeter is jacketed, and can be cooled to zero or heated to 88°, at which temperature a mixture of molecular proportions of dextrose and lævulose becomes optically inactive (J. Amer. Chem. Soc. 1896, 81).

Witte recommends that the following determinations and tests should be made in order to ascertain the purity or otherwise of honey, a solution containing 1 part by weight of the honey to two parts of water being used: Total nitrogen (Kjeldahl); tannin precipitate; polarisation before and after inversion. Leys' reaction (*v. supra*) and Fiehe's test with resorcinol and hydrochloric acid for the presence of added invert sugar. The quantity of water present should not exceed 20 p.c., whilst the acidity of native (German) honey usually lies between 0·06 and 1·2 p.c. The quantity of ash is generally from 0·1 to 0·35 p.c., but may sometimes be as little as 0·065 p.c. The sucrose should not exceed 6 p.c., a larger amount than this indicating that the honey is 'unripe,' that the bees have been fed on sucrose, or that the honey is adulterated. Sucrose may be inverted by means of honey at a suitable temperature. The nitrogenous substances vary in amount from 0·25 to 0·55 p.c.; artificial honey seldom contains more than 0·22 p.c. of nitrogenous substances (Zeitsch. Nahr. Genussm. 1909, 18, 625; 1911, 21, 305; *cf.* Bruhns, Chem. Zeit. 1921, 45, 661 *et seq.*). The J. Soc. Chem. Ind. 1911, 30, 702, gives a useful bibliography of honey and its chemistry.

HONTHIN *v.* SYNTHETIC DRUGS.

HOPEÏNE is a crystalline alkaloid said to be contained in wild American hops. It melts below 100° and partially sublimes below 160°. It is doubtful, however, whether it really exists (Ladenburg, Ber. 1886, 19, 783; J. Pharm. Chim. [v.] 12, 460; Williamson, Chem. Zeit. 1886, 10, 20, 38, 207, 238, 491).

HOPEITE. Hydrated zinc phosphate,

$$Zn_3(PO_4)_2{\cdot}4H_2O$$

crystallised in the orthorhombic system. The crystals are remarkable in consisting of an intimate zonal intergrowth of two modifications —*α*-hopeite and *β*-hopeite—differing in their optical characters and in the rate at which water is expelled by heat. They are colourless, white, or brownish; sp.gr. 3·0–3·1; H. 3¼. For many years hopeite was known only as a rare mineral from the zinc mine of Altenberg, or Vieille Montagne, between Liége and Aachen; but in 1907 it was found finely crystallised and in considerable quantity in a cave with bone-breccia and associated with ores of zinc and lead at Broken Hill in North-Western Rhodesia. In 1916 it was incorrectly described under the new name bibbenite from the Hudson Bay zinc mine near Salmo in British Columbia.

Parahopeite, from Broken Hill, Rhodesia, has the same composition as hopeite, but the crystals are anorthic. L. J. S.

HOPOGAN. A trade name for magnesium perhydrol.

HOPS *v.* BREWING.

HORDEIC ACID *v.* DODECATOIC ACID.

HORDEIN *v. Barley*, art. BREWING.

HORDENINE (p-*Hydroxyphenylethyldimethylamine*) $C_{10}H_{15}NO$ was discovered by Léger (Compt. rend. 1906, 142, 108) in malt culms, from which it is extracted by Stas' method. The ethereal solution of the alkaloid thus obtained is evaporated to dryness and the hordenine residue is purified by repeated recrystallisation from alcohol. Its constitution was determined by Léger (Compt. rend. 1906, 143, 234, 916) and by Gaebel (Arch. Pharm. 1906, 244, 435).

Hordenine has also been synthesised from phenyl ethyl alcohol (Barger, Chem. Soc. Trans. 1909, 2194; Léger, Bull. Soc. chim. 1910, [iv.] 7, 172), and by the methylation of *β-p*-methoxyphenylethylamine hydrochloride with alcoholic potash and methyl iodide at 100° (Rosenmund, Ber. 1910, 43, 306).

Properties.—Hordenine forms colourless, almost tasteless anhydrous orthorhombic prisms, m.p. 117·8° and subliming like camphor at 140°–150°. It is readily soluble in alcohol, ether, or chloroform, but sparingly so in benzene, xylene, or toluene. It is optically inactive. It is a strong base, is alkaline towards litmus and phenolphthalein, liberates ammonia from its salts, reduces acid solutions of potassium permanganate in the cold and ammoniacal solutions of silver nitrate and iodic acid on warming. It is not attacked by concentrated sulphuric acid or by potash, but readily forms soluble salts with acids. When boiled with nitric acid it yields picric acid, and when methylated and oxidised with alkaline permanganate it gives anisic acid (Léger, J. Pharm. Chim. 1907, 25, 5; Compt rend 1907, 144, 488).

Hordenine sulphate crystallises in needles and has a slightly bitter taste. It forms brown crystals with iodine, but gives no precipitate with the tannins of vegetable infusions In small doses it has a tonic action on the heart, but in toxic doses (1 2 grams per kilo) it produces the reverse effect.

It has been employed as a remedy in cases of typhoid, dysentery, enteritis, &c. It is not so energetic as digitalis, sparteine, or strophanthus, but is less toxic than any of these (Sabrazès and Guéreve, Compt. rend. 1908, 147, 1076; *see* also Camus, *ibid.* 1906, 142, 110, 237).

Hordenine methiodide, which probably possesses a similar physiological action to that of adrenaline, has been synthesised from *p*-methoxyphenylethylamine by treatment with methyl iodide, an almost quantitative yield being obtained. It crystallises in colourless prisms, m.p 229 230° (Rosenmund, *l.c.*). Other organic and inorganic compounds of hordenine have also been obtained (Léger, *l.c.*, and Compt. rend. 1907, 144, 208).

Detection.- A few drops of hordenine are dissolved in a few c.c. of acetic acid and boiled with a few drops of formaldehyde; 3 c.c. of sulphuric acid is now added, when a green coloration is produced (Denigès, Bull. Soc. chim. 1908, [iv.] 3, 786).

1 c.c. of 1 p.c. hordenine sulphate solution is boiled with an equal volume of urotropine solution of the same strength, and 2 c.c. of strong sulphuric acid, a fine emerald-green colour is produced even with 0·0001 gram of hordenine sulphate (Labat, J. Pharm. Chim. 1909, 29, 433).

HOREHOUND *v.* MARRUBIUM.

HORNBLENDE. An important rock-forming mineral belonging to the monoclinic series of the amphibole group, consisting mainly of metasilicates of calcium, magnesium, and iron. The name hornblende is sometimes applied to the group itself, which includes the useful minerals asbestos (*q.v.*), nephrite (*v.* Jade), and crocidolite (*q.v.*). More usually, however, it is restricted to the darker-coloured (green, brown, black) aluminous varieties, the composition of which is expressed by mixtures in various proportions of the molecules $Ca(Mg,Fe)_3(SiO_3)_4$, $(Mg,Fe)(Al,Fe)_2SiO_6$, and $NaAl(SiO_3)_2$. It forms part of many kinds of igneous rocks, *e.g.* hornblende-granite, syenite, basalt, &c., and crystalline schists, *e.g.* hornblende-schist. L. J. S.

HORNFELS *v.* HORNSTONE.

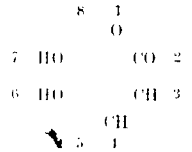
HORN LEAD *v.* LEAD.

HORN QUICKSILVER. *Calomel v.* MERCURY.

HORNSILVER. Native silver chloride *v.* CERARGYRITE; SILVER.

HORNSTONE and **HORNFELS.** Names applied to a variety of hard and tough, fine-grained and compact, splintery, siliceous rocks with a horny appearance, which have generally been formed by the baking action of igneous rock-masses on surrounding sedimentary rocks (sandstones, grits, shales, slates, &c.). They frequently show a banded structure representing the original bedding planes, but they do not break along these directions. The name hornstone is more usually applied by mineralogists to the highly siliceous kinds, and regarded as a variety of quartz allied to flint, chert, novaculite, and jasper; whilst the German name hornfels is applied by petrographers to materials more of the nature of rocks, *e.g.* biotite-hornfels, andalusite-hornfels, tourmaline-hornfels, calcsilicate-hornfels, &c, the last-named having been produced by the thermal metamorphism of impure siliceous limestones. The Swedish *Hälleflinta* (meaning rock-flint) is also very similar in character; this may in some cases represent an altered felsitic lava, but in others it does not differ from hornfels. These materials are used as hones (*v.* Whetstone). L. J. S.

HORSE-CHESTNUT. *Marronier d'Inde*, Fr.; *Rosskastanie*, Ger. The well-known horse-chestnut tree, *Æsculus hippocastanum* (Linn.), is a native of Persia and Northern India, and was introduced into Europe in the sixteenth century. The bark contains, besides tannin, fat, and other common substances, a glucoside *æsculin* and a little of its fission product *æsculetin.* On account of its blue fluorescence in aqueous solution, still recognisable at 1 : 15,000,000, the substance attracted early attention, and was first termed Schillerstoff in German. It has been chiefly examined by Rochleder and Schwarz (Annalen, 1853, 87, 186; 88, 356). Æsculin is obtained by extracting the bark (best collected in March) with boiling water, precipitating the extract with lead acetate, removing the excess of lead from the filtrate with hydrogen sulphide, and then concentrating until crystallisation begins. After a few days the crystals are collected and recrystallised first from alcohol and then from boiling water. Æsculin, $C_{15}H_{16}O_9,1\frac{1}{2}H_2O$, forms white needles of slightly bitter taste, which lose their water of crystallisation at 120°–130° and melt at 200°–202°; it dissolves in 600 parts of cold, and 12·5 parts of boiling water, in 100 parts of cold, and 24 parts of boiling alcohol. As in many cases, acids abolish the fluorescence. Agitation with a little nitric acid gives a yellow solution, turning deep red with ammonia (Sonnenschein, Ber. 1876, 9, 1182). The solution in a few drops of concentrated sulphuric acid is coloured deep violet by gradual addition of sodium hypochlorite solution. Bromine furnishes crystalline dibromoæsculin, $C_{15}H_{14}O_9Br_2$, m.p. 194°, sodium amalgam amorphous hydroæsculin; crystalline penta-acetyl and benzoyl derivatives are known. Emulsin and warm dilute mineral acids hydrolyse to dextrose and *æsculetin* (Zwenger, Annalen, 1854, 90, 65). Æsculetin and glucosan are formed by heating æsculin to 230°. Æsculetin, $C_9H_6O_4.H_2O$, may be purified by precipitation in alcoholic solution with lead acetate, washing the lead compound with alcohol and regenerating with hydrogen sulphide. It crystallises in needles, m.p. 270°, little soluble in cold, moderately in hot water, readily in hot alcohol, hardly in ether. It reduces Fehling's and ammoniacal silver solutions. It is 6 : 7-dihydroxycoumarin as shown by the synthesis



from hydroxyhydroquinone aldehyde, acetic anhydride, and sodium acetate (Gattermann and Kobner, Ber. 1899, 32, 288). Æsculetin has in aqueous solution only a very slight fluorescence. For reduction products, *see* Liebermann and Lindenbaum (Ber. 1902, 35, 2919); for *æsculose*, Sigmund (Monatsh. 1910, 31, 657); for the microchemistry of æsculin, Tunmann (Chem. Soc. Abstr. 1917, ii. 59).

The bark of the horse-chestnut further contains the glucoside *fraxin* $C_{16}H_{18}O_{10}$, also present in the bark of the ash. It is hydrolysed to dextrose and *fraxetin* $C_9H_5O_4OMe$, a methoxy æsculetin (Körner and Biginelli, Gazz. chim. ital. 1891, 21, ii. 452). *Scopolin*, in the root of *Scopolia* sp., in *Atropa belladonna*, and in other *Solanaceæ*, is a glucoside of scopoletin or 7-hydroxy-6-methoxy coumarin, and therefore of æsculetin monomethyl ether (Moore, Chem. Soc. Trans. 1911, 99, 1043; in this paper an account of the earlier literature is given; a different system of numbering the substituents is employed). Scopoletin has sometimes been confused with æsculetin; it occurs free in *Gelsemium sempervirens*.

The cotyledons contain two little-known glucosides and other derivatives (Rochleder, J. pr. Chem. [i.] 87, 1; [i.] 101, 415). The leaves quercitrin, the flowers quercetin (Rochleder, J. 1859, 522).

Horse-chestnuts are rich in carbohydrates, and can be used for the production of alcohol and acetone by fermentation; the yield of alcohol may be 11·5–12 p.c. of the nuts as picked. *Cf.* J. Soc. Chem. Ind. 1919, 41T. Bitter and harmful principles (saponins) can be extracted by boiling water, and then the nuts constitute a valuable cattle food; they have even been incorporated in bread (*cf.* Dechambre, Compt. rend. Acad. Agric. 1917, 3, 927). Entire fresh chestnuts contain about 45 p.c. of water, and air dry about 11 p.c. The following percentage analysis (Baker and Hulton, Analyst, Nov. 1917) refers to peeled and grated nuts dried at 55°: moisture, 1·85–3·5; ash, 2·45–2·9; ether extract (oil), 5·0–7·2; protein (N × 6·25), 7·25–10·8; reducing sugars as dextrose, 1·6–9·1; cane-sugar, 7·27–17·5; starch (Lintner), 21·9–47·8; starch (taka diastase), 15·2–39·0; pentosans, 4·75–5·44; crude fibre, 2·0–2·6; matter soluble in cold water, 32·5–48·4. The oil, at one time used in medicine, has been examined by Stillesen (Chem. Zeit. 1909, 33, 497), G. Masson (Bull. Sci. Pharmacol. 1918, 25, 65; Chem. Soc. Abstr. 1918, i. 518). G. B.

HORSE FAT. The fat obtained from different parts of the horse is a pale yellow to orange semi-solid mass with an unpleasant odour. On standing it separates into a solid and liquid portion, the latter being known in commerce as *horse oil*, not to be confused with *horse foot oil*. Both the fat and the oil have drying properties, which render them unsuitable for lubricating purposes. The fat does not appear to contain any stearic acid (Hehner and Mitchell), but contains about 10 p.c. of linolic acid. It melts at about 34°–39°, and has an iodine value varying from about 75–90 according to the part of the animal whence it was derived (*cf.* Heiduschka and Steinruck, J. pr. Chem. 1921, 102, 241).

Horse fat is used as a substitute for lard in some parts of Europe. Its use is claimed in Eng. Pat. 25046, 1905, as a medium for coating calcium carbide in the production of acetylene. C. A. M.

HORSE-RADISH. The root of *Cochlearia Armoracia* (Linn.), used as a condiment. Its pungent flavour is due to the presence of *iso*butyl isothiocyanate C_4H_9NCS. The root contains—

Water	Nitrogenous substances	Fat	N-free extract	Crude fibre	Ash	Organic sulphur
76·7	2·7	0·3	15·9	2·8	1·5	0·08

The following is an analysis of the ash of horse-radish:—

Per cent of ash in the dry subst	K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	SiO_2	Cl
7·1	30·8	4·0	8·2	2·9	1·9	7·8	30·8	12·7	0·9

H. I.

HUANTAJAYITE *v.* HALITE.

HUASCOLITE *v.* ZINC-BLENDE.

HÜBNERITE *v.* WOLFRAMITE.

HULSITE. A black, opaque, orthorhombic (?) mineral originally described as a hydrous borate of ferrous and ferric iron and magnesium, but subsequently found to contain some tin (SnO_2, 7·07 p.c. in a sample with a considerable amount of insoluble gangue), the formula being given as $12(Fe,Mg)O{\cdot}2Fe_2O_3{\cdot}SnO_2{\cdot}3B_2O_3{\cdot}2H_2O$. It occurs as small crystals and tabular masses in a metamorphic limestone, near the contact of this rock with granite, at Brooks Mountain, Seward Peninsula, Alaska, and is associated with magnetite and tin-ore. L. J. S.

HUMIC ACID. The substance produced by the decay of vegetable matter and found in the soil. Various humic acids have been described; an octobasic acid $C_{60}H_{54}O_{27}$ (Detmer, J. 1873, 844); an acid $C_{24}H_{10}O_{10}$ (Thenard, J. 1873, 844); an acid $C_{28}H_{22}O_{18}$, from brown coal (Hoppe, Zeitsch. physiol. Chem. 13, 108); and an acid

$C_{46}H_{16}O_{25}$ from coal (John, Zeit. Kryst. Min. 23, 289). According to Robertson, Irvine, and Dobson (Bio-Chem. J. 1907, 2, 458), the natural humic acid from peat varies greatly in composition, according to the method of preparation. The artificial acid from sugar, according to them, has the composition $C_{39}H_{32}O_{14}$, but Berthelot and André (Compt. rend. 112, 916) state that this acid is tribasic and has the composition $C_{18}H_{16}O_7$. Humic acid is capable of absorbing ammonia, which is then removed by the acid of sprouting seeds, humic acid being regenerated (Borntraeger, Chem. Zentr. 1900, ii. 1202) Gautreau, Charbonnier, and Serrant (Eng. Pat 22028; J. Soc. Chem. Ind. 1895, 977) treat peat or vegetable refuse with dilute sulphuric acid, to produce humic acid. The mass after the removal of the liquid matter is treated with excess of lime, potassium sulphate is added, and the resulting substance sold as a manure.

HUMULON (*a-hop-bitter acid* or *lupulic acid*) $C_{21}H_{30}O_5$. A substance contained in lupulin, one of the bitter principles of hops It may be obtained by repeated precipitation as the lead salt from a methyl alcoholic extract of lupulin and may be purified by crystallisation of its combination with *o*-phenylenediamine. With it forms slender yellow needles, m p. 115°–117°.

Humulon melts at 66°, $[\alpha]_D^{20}$ 212 in 96 p.c alcohol, - 232·2° in benzene; is odourless and almost tasteless. Reduces ammoniacal silver oxide in the cold and gives a deep reddish-violet colour with alcoholic ferric chloride Gives crystalline precipitates with salts of copper and lead. Subjected to hydrolysis forms *iso*-butyraldehyde, acetic acid, humulic acid, an unsaturated acid, $C_6H_{10}O_2$, b p. 105° 10 mm., giving characteristic zinc, cadmium, and silver salts, and a bitter resin (35–40 p c. of the whole) *Humulic acid* $C_{15}H_{22}O_4$ (*cf* Lintner and Schnell, Zeitsch. ges Brauw. 1904, 27, 668) is only feebly acidic, and is probably not a real carboxylic acid; it contains a ketonic group, and therefore behaves as an enol; is unsaturated, and may be reduced by palladium and hydrogen to *dihydrohumulic acid* $C_{15}H_{24}O_4$, flat needles and leaflets, m.p. 125°–126° (*phenylhydrazone*, faintly yellow, short prisms, m.p. 133°–134°).

Humulon may also be catalytically hydrogenated, whereby it suffers fission into an *acid* $C_{16}H_{24}O_5$ and β-methylbutane. $C_{21}H_{30}O_5+3H_2=C_{16}H_{24}O_5+C_5H_{12}$. The acid forms yellow crystals, m.p. 123°–125°, behaves as a monobasic acid; forms a *tetrabenzoate* $C_{16}H_{20}O_5 \cdot Bz_4$ in colourless flat prisms, m.p. 168°. Alcoholic solutions give a dark blue coloration with lead acetate. A warm methyl-alcoholic solution in a current of air yields a *dihydroxyquinone* $C_{16}H_{22}O_5$; slender, red needles, m.p. 63°–64°, which condensed with *o*-phenylendiamine gives a dark red azine $C_{22}H_{26}O_3N_2$, m p. 109° Wöllmer, Ber. 1916, 49. 780).

HUNGARIAN TURPENTINE *v.* OLEO-RESINS.

HUNGARY BLUE. *Cobalt blue v.* PIGMENTS.

HUNGARY GREEN. *Malachite green v.* PIGMENTS.

HUTCHINSONITE. Sulph-arsenite of thallium, lead, silver, and copper

$$(Tl,Ag,Cu)_2S \cdot As_2S_3+PbS\ As_2S_3$$

crystallised in the orthorhombic system, and one of the few minerals that contain thallium (18–25 p.c.) as an essential constituent. It is of rare occurrence as minute, red, transparent crystals in the white, crystalline dolomite of the Binnenthal in Switzerland. L. J. S.

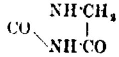
HYACINTH or **JACINTH.** A name loosely applied to several kinds of gem-stones of a yellowish-red or red shade, but more usually to zircon (*q.v.*). Other stones of similar colour to which the name is sometimes applied include: ferruginous quartz from Santiago de Compostella in the north of Spain (Compostella hyacinth); hessonite (*v.* garnet); brown idocrase or vesuvianite from Vesuvius; yellowish-red spinel from Minas Novas, Brazil; topaz from Brazil; and reddish-brown corundum (Oriental hyacinth). The *ὑάκινθος* or *hyacinthus* of the ancients was, however, a blue or purple stone, probably corundum (sapphire), or perhaps amethyst.

L. J. S.

HYÆNASIC ACID $C_{24}H_{48} \cdot COOH$, m.p. 77·5°, is found as a glyceride in the anal glandular pouches of the striped hyæna (Carius, Annalen, 129, 168)

HYALINE CORUNDUM *v.* ALUMINIUM.

HYALITE *v.* OPAL.

HYDANTOIN, *glycolylcarbamide* 

$$CO\begin{cases}NH \cdot CH_2\\ \qquad\ |\\ NH \cdot CO\end{cases}$$

is found together with allantoin in the leaf buds of *Platanus orientalis* (Linn.) (Schulze and Barbieri, Ber. 1881, 14, 1834); and also in beet juice (v. Lippmann, Ber. 1896, 29, 2652). It is prepared (1) by reducing allantoin or alloxanic acid with concentrated hydrogen iodide at 100° (Baeyer, Annalen, 1864, 130, 158); (2) by the action of excess of alcoholic ammonia on bromacetylurea at 100° (Baeyer, Ber. 1875, 8, 612); (3) by the condensation of sodium dihydroxytartrate and carbamide in the presence of hydrochloric acid at 50°–60° (Anschütz, Annalen, 1889, 254, 258); (4) by the condensation of glyoxal and carbamide in the presence of hydrochloric acid (Siemonsen, Annalen, 1904, 333, 101); (5) from ethyl hydantoate by heating at 135° for 7 hours, or by warming with 25 p.c. hydrochloric acid (Harries and Weiss, Ber. 1900, 33, 3418), or by heating with alcoholic ammonia at 100° (Harries, Annalen, 1908, 361, 69); the ethyl hydantoate is prepared by the condensation of the hydrochloride of the ethyl ester of glycine with potassium cyanate (Harries and Weis, *l.c.*) or by the interaction of glycollic ester and ethyl sodiocarbonate (Diels and Heintzel, Ber. 1905, 38, 305). It may be prepared from hippuric acid by converting it into 3-benzoyl-2-thiohydantoin (Johnson and Nicolet, J. Amer. Chem. Soc. 1911, 13, 1973) and then desulphurising this compound with an aqueous solution of chloracetic acid (Johnson and Bengis, *ibid.* 1913, 35, 1605).

Hydantoin crystallises in colourless needles, m.p. 216° (Schulze and Barbieri, Anschütz, *l.c.*); 217°–220° (Harries and Weiss, *l.c.*); its heat of combustion at constant volume is +312·4Cal., and heat of formation +109Cal. (Matignon, Ann. Chim. 1893, [vi.] 28, 70). Its dissociation constant *Ka* is $7{\cdot}59 \times 10^{-10}$ (Wood, Phil. Trans. 1906, 1833). It is sparingly soluble in cold, readily so in hot water, and the solution has a sweetish taste. Hydantoin is not attacked by ammonia, hydrochloric, or dilute nitric acid;

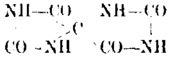
when boiled with baryta water it is converted into the barium salt of *hydantoic acid*

$NH_2\cdot CO\cdot NH\ CH_2\cdot CO_2H$

the heat of combustion of which is 308·9Cal. and heat of formation +181·6Cal. (Matignon, *l.c.*), m.p. 179°–180°.

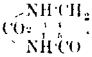
The *silver derivative* $C_3H_3O_2N_2Ag,H_2O$ is precipitated by silver nitrate from an ammoniacal solution of hydantoin.

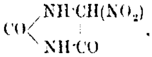
Spiro 4 : 4 dihydantoin



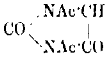
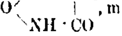
$$\begin{matrix}NH-CO & & NH-CO\\ & >C< & |\\ CO-NH & & CO-NH\end{matrix}$$

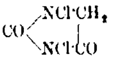
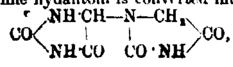
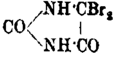
prepared by boiling 5-amino-4-hydroxy-4 : 5-dihydrouric acid with concentrated hydrochloric acid, crystallises in stout rhombohedra which only slowly blacken and decompose above 400°. It is remarkably stable towards acids, and is not attacked by alkaline permanganate; it is converted by hot concentrated aqueous barium hydroxide into allantoin. It is the parent substance of hypocaffeine (1 : 7 : 9-*tri-methyl-spiro-4 : 4-hydantoin*) (Biltz and Heyn, Annalen, 1916, 413, 38).

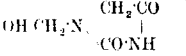
Substituted derivatives of hydantoin are referred to the ring  $CO<\begin{matrix}NH\cdot CH_2\\ |\\ NH\cdot CO\end{matrix}$.

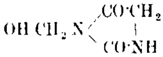
Nitrohydantoin  $CO<\begin{matrix}NH\cdot CH(NO_2)\\ |\\ NH\cdot CO\end{matrix}$, prepared by the action of nitric acid on hydantoin, forms shining crystals, melting and decomposing at 170° (Franchimont and Klobbie, Rec. trav. chim 1888, 7, 12).

4-Aminohydantoin hydrochloride, prepared by the action of concentrated hydrochloric acid on triacetylaminohydantoin, has m.p 218°–222° (decomp.). Silver oxide reacts with it to yield 3-*silver-4-aminohydantoin* and aqueous potassium cyanate reacts with it with formation of allantoin (Biltz and Giesler, Ber. 1913, 46, 3423).

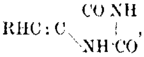
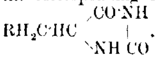
1 : 3-Diacetylhydantoin  $CO<\begin{matrix}NAc\cdot CH_2\\ |\\ NAc\cdot CO\end{matrix}$, obtained by the action of acetic anhydride on hydantoin, has m.p. 104°–105°, and yields 3-*acetylhydantoin*  $CO<\begin{matrix}NAc\cdot CH_2\\ |\\ NH\cdot CO\end{matrix}$, m.p. 143°–144°, when boiled with water, and this forms a sparingly soluble *lead salt* (Harries and Weiss, Annalen, 1903, 327, 355; Siemonsen, Annalen, 1904, 333, 101).

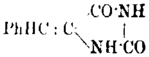
Dichlorohydantoin  $CO<\begin{matrix}NCl\cdot CH_2\\ |\\ NCl\cdot CO\end{matrix}$ obtained in the form of lustrous crystalline leaves, m.p. 120°–121°, by the action of chlorine on an aqueous solution of hydantoin, has the characteristic properties of a chlorimino compound (Harries and Weiss, Annalen, 1903, 327, 355; Siemonsen, Annalen, 1904, 333, 101; Biltz and Behrens, Ber. 1910, 43, 1984). Attempts to prepare bromine derivatives of hydantoin have been unsuccessful; by the action of ½ molecule of bromine hydantoin is converted into iso*allituric acid*  $CO<\begin{matrix}NH\cdot CH-N-CH_2\\ |\qquad\quad |\\ NH\cdot CO\quad CO\cdot NH\end{matrix}>CO$, m.p. 258°–260°, when a larger proportion of bromine is employed, parabanic acid (oxalylcarbamide), is formed, the bromo derivative  $CO<\begin{matrix}NH\cdot CBr_2\\ |\\ NH\cdot CO\end{matrix}$ being probably first produced.

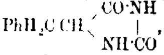
Condensation with aldehydes. Hydantoin condenses with formaldehyde (1–3 mols.) in aqueous solution to form *hydroxymethylhydantoin*  $OH\ CH_2\cdot N<\begin{matrix}CH_2\cdot CO\\ |\\ CO\cdot NH\end{matrix}$

or  $OH\ CH_2\ N<\begin{matrix}CO\cdot CH_2\\ |\\ CO\cdot NH\end{matrix}$

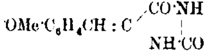
m.p. 125°–135°, it yields *chloromethylhydantoin* $C_4H_5O_2N_2Cl$, m.p. 150°–157°, when treated with phosphorus pentachloride or concentrated hydrochloric acid. When hydantoin is warmed with formaldehyde in the presence of acids more complex products are obtained (Behrend and Niemeyer, Annalen, 1909, 365, 38).

Hydantoin condenses with aromatic aldehydes in the presence of glacial acetic acid and sodium acetate to form compounds of the type  $RHC:C<\begin{matrix}CO\cdot NH\\ |\\ NH\cdot CO\end{matrix}$, which, on reduction, yield the corresponding 4-*aryl*-substituted hydantoin  $RH_2C\cdot HC<\begin{matrix}CO\cdot NH\\ |\\ NH\ CO\end{matrix}$. The following compounds are described:—

Benzylidenehydantoin  $PhHC:C<\begin{matrix}CO\cdot NH\\ |\\ NH\cdot CO\end{matrix}$

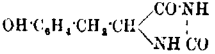
m.p. 220°, yields 4-*benzylhydantoin* (*phenylalaninehydantoin*)  $PhH_2C\ CH<\begin{matrix}CO\cdot NH\\ |\\ NH\cdot CO\end{matrix}$, m.p. 188°–190° on reduction, from which phenylalanine is obtained by boiling with baryta water (Ruhemann and Stapleton, Phil. Trans. 1900, 246). Johnson and Bates (J. Amer. Chem. Soc. 1915, 37, 383) record two isomeric modifications of benzylidenehydantoin: the ordinary form (*cis*), m.p. 220°, and a *trans*-form, m.p. 246°, which crystallises in aggregates of distorted needles (*cf.* Komatsu, Mem. Coll. Sci. Eng. Kyoto, 1912, 5, 13).

Anisylidenehydantoin



$$OMe\cdot C_6H_4CH:C<\begin{matrix}CO\cdot NH\\ |\\ NH\cdot CO\end{matrix}$$

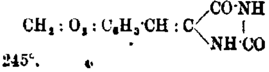
m.p. 243°–244° (decomp.) yields a *bromo* derivative, m.p. 247°; and on reduction with hydrogen iodide forms 4-*p-hydroxybenzylhydantoin* (*tryosinehydantoin*)



$$OH\cdot C_6H_4\cdot CH_2\cdot CH<\begin{matrix}CO\cdot NH\\ |\\ NH\ CO\end{matrix}$$

m.p. 257°–258°, from which *tyrosine* is obtained by prolonged boiling with hydrogen iodide. The tyrosinehydantoin, m.p. 275°–280°, described by Blendermann (Bied. Zentr. 1883, 209) is probably the optically active isomeride of this compound.

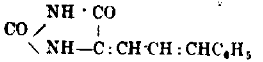
Piperonylidenehydantoin



$$CH_2:O_2:C_6H_3\cdot CH:C<\begin{matrix}CO\cdot NH\\ |\\ NH\cdot CO\end{matrix}$$

m.p. 245°.

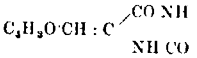
4-Cinnamylidenehydantoin



$$CO\begin{cases}NH\cdot CO\\ NH-C:CH{\cdot}CH:CHC_6H_5\end{cases}$$

crystallises from hot glacial acetic acid in clusters of canary-yellow needles which melt at 272°–273° to a red oil (decomp.) (Johnson and Wrenshall, J. Amer. Chem. Soc. 1915, 37, 2133).

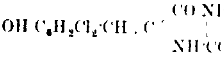
Furfurylidenehydantoin



$$C_4H_3O{\cdot}CH:C\begin{cases}CO{\cdot}NH\\ NH{\cdot}CO\end{cases}$$

m.p. 232°.

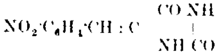
3 : 5-*Dichloro-4-hydroxybenzylidenehydantoin*



$$OH{\cdot}C_6H_2Cl_2{\cdot}CH:C\begin{cases}CO{\cdot}NH\\ NH{\cdot}CO\end{cases}$$

m.p. 300°.

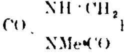
p-Nitrobenzylidenehydantoin

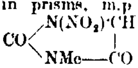


$$NO_2{\cdot}C_6H_4{\cdot}CH:C\begin{cases}CO{\cdot}NH\\ NH{\cdot}CO\end{cases}$$

m.p. 254° (Wheeler and Hoffmann, Amer. Chem. J. 1911, 45, 368). *See* Johnson and Brautlecht (J. Biol. Chem. 1912, 12, 184) for the preparation of 1-*phenyl-4-paranitrobenzalhydantoin* and allied compounds from *thiohydantoin* derivatives.

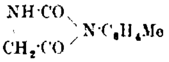
Alkyl and aryl substituted derivatives.

1-*Methylhydantoin*  $CO\begin{cases}NH\cdot CH_2\\ NMe{\cdot}CO\end{cases}$ by methylating hydantoin by means of methyl iodide, potassium hydroxide, and methyl alcohol at 100° (Franchimont and Klobbie, Rec. trav. chim. 1889, 8, 289); from methylcarbamide and glycine (Guareschi, Chem. Zentr. 1892, i. 140); crystallises in prisms, m.p. 182°. The *nitro* derivative



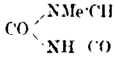
$$CO\begin{cases}N(NO_2){\cdot}CH_2\\ NMe-CO\end{cases}$$

has m.p. 168° (Franchimont and Klobbie, *l.c.*). 1-*p-tolylhydantoin*



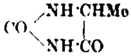
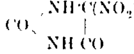
$$\begin{matrix}NH{\cdot}CO\\ CH_2{\cdot}CO\end{matrix}\Big>N{\cdot}C_6H_4Me$$

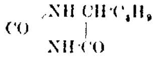
from *p*-tolylcarbamide and glycine (Quenda, Chem. Zentr. 1892, i. 140); it has m.p. 206°.

3-*Methylhydantoin*  $CO\begin{cases}NMe{\cdot}CH_2\\ NH{\cdot}CO\end{cases}$, prepared **(1) by fusing sarcosine and urea** (Huppert, Ber. 1873, 6, 1278; Horbaczewski, Monatsh. 1887, 8, 586); **(2) by passing cyanogen chloride through fused sarcosine** (Traube, Ber. 1882, 15, 2111); **(3) by heating caffuric acid with baryta water** (Fischer, Annalen, 1882, 215, 286); or (4) by reducing 3-methylallantoin with hydrogen iodide (Fischer and Ach, Ber. 1899, 32, 2748) forms soluble prisms, m.p. 156°; the *silver* derivative $AgC_4H_5N_2O_2$ is crystalline.

3-*Phenylhydantoin* from phenylglycine and urea has m.p. 191°; 3-*tolylhydantoin* has m.p. 210° (Schwebel, Ber. 1877, 10, 2045; 11, 1128).

Homologues of hydantoin containing the substituent in position 4- are most numerous; and are prepared by the following general methods: (1) by interaction between the cyanohydrin of an aldehyde and carbamide (Pinner, Ber. 1887, 20, 2351; 21, 2320; 22, 685); (2) by the action of dilute hydrochloric acid on the hydantoic acid obtained by evaporating to dryness a solution of an α-amino acid and potassium cyanate (Dakin, Amer. Chem. J. 1910, 44, 48); or by the interaction of carbamide, the α-amino acid and baryta water (Lippich, Ber. 1908, 41, 2953); (3) by reducing the compound obtained by the condensation of hydantoin and an aromatic aldehyde (Wheeler and Hoffmann, *l.c.*).

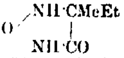
4-*Methylhydantoin* (*lactylurea*)  $CO\begin{cases}NH{\cdot}CHMe\\ NH{\cdot}CO\end{cases}$ (Heintz, Annalen, 1873, 169, 125; Urech, Ber. 1873, 6, 1113), m.p. 140° or 145°. The *nitro* derivative  $CO\begin{cases}NH{\cdot}C(NO_2)Me\\ NH{\cdot}CO\end{cases}$ m.p. 148° (Franchimont and Klobbie, Rec. trav. chim. 1888, 7, 13). 4-*isoButylhydantoin*

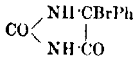


$$CO\begin{cases}NH{\cdot}CH{\cdot}C_4H_9\\ NH{\cdot}CO\end{cases}$$

has m.p. 209°–210° (Pinner and Lifschütz, Ber. 1887, 20, 2351), 212° (Lippich, *ibid.* 1908, 41, 2953). *l*-4-*isoButylhydantoin* has m.p. 212°, $[\alpha]_D^{20°} -68{\cdot}2°$ in normal sodium hydroxide solution, becoming zero in 30 hours owing to the enol-keto desmotropy of the group

$$CH{\cdot}CO \rightleftarrows C:C{\cdot}OH.$$

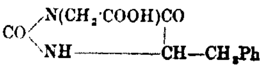
4 : 4-*Methylethylhydantoin*  $CO\begin{cases}NH{\cdot}CMeEt\\ NH{\cdot}CO\end{cases}$ has m.p. 172°–173°, and $[\alpha]_D^{20} + 32°$, and this is constant in normal sodium hydroxide solution (Dakin, *l.c.*). 4-*Phenylhydantoin*, m.p. 178°. The *acetyl* derivative has m.p. 145° (Pinner, *l.c.*); the *bromo* derivative



$$CO\begin{cases}NH{\cdot}CBrPh\\ NH{\cdot}CO\end{cases}$$

melts above 200°, and is decomposed by hot water, yielding 4-*hydroxy-4-phenylhydantoin* (Gabriel, Annalen, 1906, 350, 118). 4 : 4-*Phenylethylhydantoin* (*nirvanol*), m.p. 197°, and its sodium salt are hypnotics; the free acid is tasteless, the sodium salt has a bitter taste (Wernecke, Deut. Med. Woch. 1916, 42, 1193; Piotrowski, Chem. Zentr. 1916, 11, 1182; from Munch. Med. Wchschr. 63, 1572; Farb. vorm. M.L. and B. Swiss, 72, 561). 4 : 4-*Phenylpropylhydantoin* is also a soporific, m.p. 170° (Farb. vorm. M.L. and B. Swiss, 74, 189, and 79, 190). For the preparation of 4 : 4-disubstituted hydantoins which have soporific properties, *see* Chemische Fabrik von Heyden, D. R. PP. 309508, 310426.

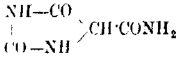
Phenylalanylglycinehydantoin (4-benzylhydantoin-1-acetic acid)



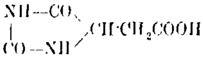
$$CO\begin{cases}N(CH_2{\cdot}COOH)CO\\ NH-CH-CH_2Ph\end{cases}$$

polypeptide hydantoin, has m.p. 184°–185°, and crystallises in flat prisms or rhombic plates (Johnson and Bates, J. Amer. Chem. Soc. 1916,

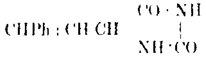
38, 1087). 4-*Methoxyphenylhydantoin* has m.p. 188°–189°. *Hydantoin-4-carboxylamine*



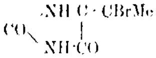
has m.p. 249° (decomp.). *Hydantoin-4-acetic acid*

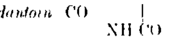


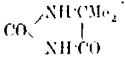
has m.p. 214°–215°. *Hydantoin-4-propionic acid* has m.p. 165°. *Hydantoin-4-β-bromopropionic acid* has m.p. 228°–230°; *hydantoin-4-βγ-propenylic acid* has m.p. 222°–223°; *hydantoin-4-β-chloropropionic acid* forms rectangular plates, *hydantoin-4-acrylic acid* has m.p. 256°–258° (Dakin, Biochem. J. 1919, 13, 398). 4-*Cinnamylhydantoin*

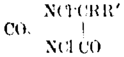


m.p. 171°–172° (Pinner and Spilker, Ber. 1889, 22, 685). 4-*Ethylhydantoin*, m.p. 117°–118°, yields 4-*bromoethylidenehydantoin*



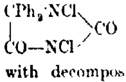
m.p. 230°–236°, on bromination; the corresponding methyl compound yields 4-*bromomethylene-hydantoin*  m.p. 241°–242° (Gabriel, Annalen, 1906, 348, 50).

4 : 4-*Dimethylhydantoin* (acetonylcarbamide)  formed by the action of hydrocyanic acid, and cyanic acid on acetone has m.p. 175°; the *nitro* derivative has m.p. 161°–162° (Urech, Annalen, 1872, 164, 264; Errera, Gazz. chim. ital. 1896, 26, 1, 210); 4 : 4-*diethylhydantoin* has m.p. 165°, and 4 : 4-*dipropylhydantoin*, m.p. 199° (Errera, *l.c.*) By the action of sodium hypochlorite and free hypochlorous acid on 4 : 4-disubstituted hydantoins, the corresponding 1 : 3-*dichloro* compounds



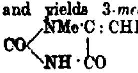
are obtained. These compounds can be crystallised from chloroform, but are decomposed by water, alcohol, or hydrogen iodide, regenerating the original hydantoin (Biltz and Behrens, Ber. 1910, 43, 1984).

1 : 3-*Dichloro-4 : 4-diphenylhydantoin*

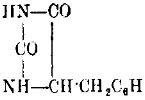


has m.p. 164° with decomposition, it yields **4 : 4-*diphenyl-1 : 3-dimethylhydantoin*** when treated with methyl sulphate.

1-***Methyl-4-phenylhydantoin*** has m.p. 161°–162° (Pinner, Ber. 1888, 21, 2320). 4-*Methyl-3-ethylhydantoin* forms volatile plates (Duvillier, Bull. Soc. chim. 1895, [iii.] 13, 487).

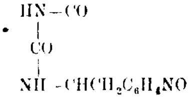
3 : 4-*Dimethylhydantoin* has m.p. 120°–121°, and yields 3-*methyl-4-bromomethylenehydantoin*  m.p. 143°–144°, by the action of bromine (Gabriel, Annalen, 1906, 348, 50).

4-*Benzylhydantoin* (inactive)



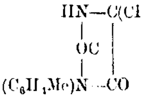
was prepared by Wheeler and Hoffmann (Amer. Chem. J. 1911, 45, 372) by heating benzal hydantoin with phosphorus and hydriodic acid. It crystallises from alcohol in lancet-shaped crystals or in prisms, m.p. 190°. Dakin and Dudley (J. Biol. Chem. 1914, 17, 35) prepared *d*- and *l-benzylhydantoin* by hydrolysis of *l*- and of *d-β-phenyl-α-uramido propionic acids* $(C_6H_5CH_2)\cdot CH(NH\cdot CONH_2)COOH$; *d-benzylhydantoin* has m.p. 181°–183°, and $[\alpha]_D + 96{\cdot}4°$ in 50 p.c. alcohol; it racemises completely on standing in alkaline solution at room temperature; *l-benzylhydantoin* has m.p. 181°–183°; on prolonged heating with concentrated acid it racemises completely; the melting point of the *r*-acid being 194°–195°.

4-*p-Nitrobenzylhydantoin*



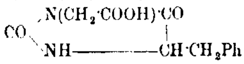
crystallises in pale yellow prisms, and has m.p. 238°–240° (decomp.). 4-*p-Aminobenzylhydantoin* has m.p. 145°; when diazotised and heated it yields tyrosine hydantoin (Johnson and Brautlecht, J. Biol. Chem. 1912, 12, 187).

4 : 4-*Dimethyl-1-o-tolylhydantoin*



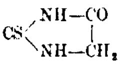
crystallises in thin prismatic plates, m.p. 172° (Bailey and McPherson, *ibid.* 1916, 11, 2526; Ber. 1908, 41, 2497).

For the synthesis of the polypeptide hydantoin, phenylalanylglycinehydantoin

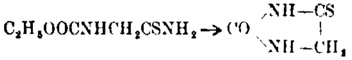


m.p. 184°–185°, *v.* Johnson and Bates (J. Amer. Chem. Soc. 1916, 38, 1087). For other derivatives of hydantoin, *see* West, J. Biol. Chem. 1918, 34, 187.

Thiohydantoins. 2-*Thiohydantoin*



was obtained by Klason (Chem. Zeit. 14, Rep. 200). It may be obtained quantitatively by hydrolysis with hydrochloric acid of 2-thio-3-acetylhydantoin or of 2-thio-3-benzoylhydantoin (produced respectively by the action of potassium thiocyanate on glycocoll or on hippuric acid in presence of acetic anhydride). It crystallises in yellow prisms, m.p. 227°–228° (decomp.). It is stable and yields stable sodium and potassium salts (Johnson and Nicolet, J. Amer. Chem. Soc. 1911, 33, 1973; *ibid.* 1913, 35, 780). 2-*Thio-1-p-tolylhydantoin*, m.p. 228°, is converted into 1-*p-tolylhydantoin* on heating with aqueous solution of chloracetic acid (*ibid.* 1912, 34, 1045). 5-*Thiohydantoin* is formed by the condensation of carbethoxyamidoacet-thioamide in presence of alkali



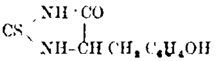
$$C_2H_5OOCNHCH_2CSNH_2 \rightarrow CO\begin{cases}NH—CS\\ NH—CH_2\end{cases}$$

It crystallises from hot water in spear-shaped twinned crystals and gradually decomposes above 200°; it hydrolyses with hydrochloric acid, yielding hydantoin and sulphuretted hydrogen (Johnson and Chernoff, *ibid.* 1912, 34, 1208)

2-*Thiohydantoin-4-propionic* acid has m.p. 165° (Johnson and Guest, Amer. Chem. J. 1912, 47, 242).

2-*Thio-4-benzalhydantoin*, microscopic needles, has m.p. 258° (slight decomp.) (Johnson and Nicolet, J. Amer. Chem. Soc. 1912, 34, 1048; *cf.* also Ruhemann and Stapleton, Chem. Soc. Trans. 1900, 77, 246)

2-*Thio-4-o-hydroxybenzylhydantoin*

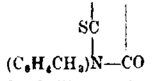


$$CS\begin{cases}NH·CO\\ NH-CH·CH_2·C_6H_4OH\end{cases}$$

m.p. 107°, is readily desulphurised by heating with 25 p.c. solution of monochloracetic acid at 140°–150°, yielding 4-*o-hydroxybenzylhydantoin* (4-*o-tyrosinehydantoin*).

Acylthiohydantoins. 2-*Thio-3-acetylhydantoin* crystallises from absolute alcohol in beautiful square tables or blocks; it melts at 175°–176° to a clear oil without effervescence. 2-*Thio-3-benzoylhydantoin* crystallises from alcohol in square plates; it melts at 165° to a clear oil without effervescence. 2-*Thio-3-acetyl-4-benzylhydantoin*, prepared by the action of ammonium thiocyanate on phenylalanine in acetic anhydride solution, has m.p. 170°. 2-*Thiol-3-acetyl-4-methylhydantoin*, prepared by the action of potassium thiocyanate on alanine in presence of acetic anhydride, crystallises in stout prisms, and has m.p. 166° (Johnson and Nicolet, J. Amer. Chem. Soc. 1911, 33, 1975; *ibid.* 1912, 34, 1041; *ibid.* 1913, 35, 1130; Amer. Chem. J. 1913, 49, 200; J. Biol. Chem. 1912, 11, 98).

4 : 4-*Dimethyl-1-o-tolyl-2-thiohydantoin*



$$\begin{array}{l}HN—C(CH_3)_2\\ \;|\qquad\;\;|\\ SC\qquad\;|\\ \;|\qquad\;\;|\\ (C_6H_4CH_3)N—CO\end{array}$$

is prepared by boiling equimolecular amounts of *o*-tolyl mustard oil and aminoisobutyrate for an hour, distilling off the alcohol, dissolving the residue in water, and precipitating the thiohydantoin by the addition of hydrochloric acid, m.p. 195·5° (Bailey and McPherson, J. Amer. Chem. Soc. 1916, 38, 2525). M. A. W.

HYDNO-CARPIC ACID, HYPOGALIC ACID, *v.* Oils, Fixed, and Fats.

HYDRACETIN. Mono-acetyl derivative of phenylhydrazine.

HYDRACRYLIC ACID *v.* Lactic acid.

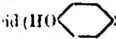
HYDRÆSCULIN *v.* Horse-chestnut.

HYDRAMIN. A trade name for a combination of *p*-phenylenediamine and quinol.

HYDRARGILLITE *v.* Gibbsite.

HYDRARGOL. Mercury succinimide $(C_2H_4·CO·CO·N)_2Hg$.

HYDRARGOTIN. Trade name for mercury tannate.

HYDRARGYROL. A mercury salt of *p*-phenol sulphonic acid (HO$SO_2—O—)_2H_g$.

HYDRARSAN. A solution of arsenic and the iodides of mercury and potassium with antipyrine.

HYDRASTINE $C_{21}H_{21}O_6N$. An alkaloid occurring together with berberine and canadine in the root of *Hydrastis canadensis* (Linn.), 'Golden Seal,' to the extent of about 1·5 p.c.

Its preparation and physical properties are described by Durand, Amer. J. Pharm. 1851, 23, 112; Perrins, Pharm. J. 1861–1862, [ii.] 3, 546; Mahla, Amer. J. Sci. 36, 57; Power, Pharm. J. 1884–1885, [iii.] 15, 297; Eijkman, Rec. trav. chim. 1886, 5, 290; Freund and Will, Ber. 1886, 19, 2797; 1887, 20, 88; Schmidt and Wilhelm, Arch. Pharm. 1888, 226, 329; and Elsa Schmidt (Amer. J. Pharm. 1919, 91, 270)

Preparation.—Hydrastine may be isolated from the mother-liquor from which the berberine salt has crystallised (*see* Berberine). This is largely diluted with water, and almost neutralised with ammonia. On evaporation, ammonium sulphate, resin, &c., separate out; these are removed, and the hydrastine precipitated from the cold liquid by ammonia. The coloured precipitate is dissolved in alcohol (Perrins, Power), or ethyl acetate (Schmidt and Wilhelm), and the colouring matter removed by digestion with animal charcoal; the alkaloid crystallises from the concentrated solution. Purification of the hydrastine is effected by repeated crystallisation from alcohol.

Some authors prefer to extract hydrastine from the root before berberine, thus, according to Freund and Will, hydrastine is most readily obtained by percolating finely powdered hydrastis root with ether, and crystallising the ethereal residue from alcohol. Elsa Schmidt employs a similar method, using benzene as the solvent.

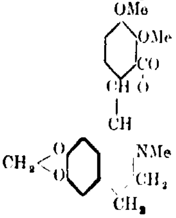
Properties.—Colourless, rhombic prisms, m.p. 132°. Insoluble in water, readily soluble in chloroform or benzene; less readily so in ether or alcohol. $[\alpha]_D$ in chloroform, −67·8° (Freund and Will); in chloroform, −63·8°; in dry alcohol, −49·8°; in 50 p.c. alcohol, +115° (Carr and Reynolds, Chem. Soc. Trans. 1910, 97, 1334). The ordinary salts of hydrastine are soluble in water, giving dextrorotatory solutions, but do not crystallise well (*cf.* Schmidt and Kerstein, Arch. Pharm. 1890, [iii.] 228, 49). Hydrastine and its hydrochloride, a hygroscopic powder, are official in the U.S.P. 1916; they are chiefly employed for the arrest of uterine hæmorrhage in doses of ¼ to ½ grain. Hydrastine is poisonous in larger doses.

Detection and estimation.—The most characteristic colour reaction of hydrastine is the production of a fluorescent solution (due to the formation of hydrastinine) by the addition of permanganate to an aqueous solution of its sulphate (*cf.* Lyons, Pharm. J. 1885–1886, [iii.] 16, 880). For other colour reactions of hydrastine, *see* Power, Pharm. J. 1885–1886, [iii.] 16, 1092; Labat, Bull. Soc. chim. 1909, [iv.] 5, 742, 745. The assay of hydrastis rhizome prescribed in the U.S.P. 1916 consists in the gravimetric estimation of the ether-soluble alkaloids, which should amount to not less than 2·5 p.c. For other methods of assay, *see* Gordin and Prescott, Arch. Pharm. 1899, 237, 439; 1901, 239, 638; van der Haar, Pharm. Weekblad. 1911, 48, 1302.

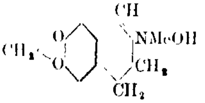
Constitution.—The oxidation of hydrastine by nitric acid yields opianic acid and hydrastinine.

$$\underset{\text{Hydrastine}}{C_{21}H_{21}O_6N} + H_2O = \underset{\text{Opianic acid}}{C_{10}H_{10}O_5} + \underset{\text{Hydrastinine}}{C_{11}H_{13}O_3N}$$

The determination of its constitution is bound up with that of these fission-products and is due mainly to the researches of Freund and Roser. The work, which has been reviewed by Freund (Annalen, 1892, 271, 311), leads to the following constitutional formulæ:—



Hydrastine



Hydrastinine

An optically-inactive stereoisomeride of hydrastine has been prepared synthetically (Hope and Robinson, Chem. Soc. Proc. 1912, 28, 17).

Hydrastinine $C_{11}H_{13}O_3N$, is prepared by the oxidation of hydrastine (Freund and Will, Ber. 1887, 20, 88), and has been synthesised by Fritzsch (Annalen, 1895, 286, 18); Decker (D. R. P. 234850, 1911), Rosenmund (Ber. Deut pharm. Ges. 1919, 29, 200)

It may also be prepared from berberine (Freund, D. R. P. 241136, 1911) and cotarnine (Pyman and Remfry, Chem. Soc. Trans. 1912, 101, 1595). Like berberine (*q.v.*), the free base occurs in two isomeric forms, in aqueous solution as the quaternary hydroxide shown above, and in the solid state as the carbinolamine (*cf.* Dobbie and Tinkler, Chem. Soc. Trans. 1904, 85, 1005). It melts at 116°–117°, crystallises from light petroleum, and is easily soluble in alcohol or ether, but sparingly so in water.

The hydrochloride, properly hydrastininium chloride, $C_{11}H_{12}O_2NCl$, is official in the U.S.P. 1916. It melts and decomposes at 210°, and is easily soluble in water, giving a neutral solution showing a blue fluorescence. It gives no turbidity with ammonia, but sodium hydroxide causes a milky turbidity which disappears on shaking, and, on keeping, the solution deposits free hydrastinine.

Canadine $C_{20}H_{21}O_4N$ occurs with crude hydrastine (*see* above), from which it may be isolated by fractional crystallisation of the nitrates, the canadine salt being less soluble. Silky needles, m.p. 132·5°, $[\alpha]_D -298°$ in chloroform (Schmidt, Arch. Pharm. 1894, 232, 136). On oxidation with iodine it is converted into berberine. By fractional crystallisation of tetrahydroberberine *d*-bromocamphorsulphonate, Gadamer (*ibid.* 1901, 239, 648) isolated a lævo-rotatory base identical with canadine, which is therefore *l*-tetrahydroberberine. Jowett and Pyman have found *l*-α-canadine methochloride in *Xanthoxylum brachyacanthum* (Chem. Soc. Trans. 1913, 103, 293). F. L. P.

HYDRAULIC CEMENTS *v.* CEMENTS.

HYDRAULIC LIME *v.* CEMENTS.

HYDRAZINES. The name 'hydrazine' was applied by Emil Fischer to the then unknown diamide $H_2N{\cdot}NH_2$, which he regarded as the parent substance of the hydrazines, a large and important class of bases which had been prepared by him and the reactions of which showed them to possess a structural formula derived from diamide by the replacement of one or two hydrogen atoms by hydrocarbon radicles. The name was intended to indicate the connection of these compounds with the azo and diazo compounds and particularly with hydrazobenzene, $C_6H_5{\cdot}NH{\cdot}NH{\cdot}C_6H_5$, the oldest known member of this class, which itself may be regarded as a symmetrically disubstituted hydrazine.

It is apparent that there are five different ways in which the four hydrogen atoms of diamide may be replaced by hydrocarbon radicles, thus: (1) $RNH{\cdot}NH_2$, (2) $RRN{\cdot}NH_2$, (3) $RHN{\cdot}NHR$, (4) $RRN{\cdot}NHR$, (5) $RRN{\cdot}NRR$, but the name hydrazine was formerly only applied to those derivatives of diamide which had the hydrocarbon radicle or radicles asymmetrically attached to the molecule, that is to say, those which are constituted in accordance with formulæ (1) and (2).

This was mainly owing to the fact that the compounds constituted as in formula (3) had already been named, as for example hydrazobenzene, $C_6H_5NH{\cdot}NH{\cdot}C_6H_5$, and that no substances of the formulæ 4 and 5 had as yet been prepared. At the present time compounds of all five classes are known, and therefore the name hydrazine is applied to all derivatives of diamide.

The hydrocarbon radicles forming the hydrazines may belong either to the aliphatic or aromatic series, although the most important members of the group belong to the aromatic series. Like the amines, they are divided into primary and secondary hydrazines, according as one or two hydrocarbon radicles are contained in them; that is to say, the primary hydrazines are constituted as in formula (1), the secondary hydrazines as in formula (2). The secondary hydrazines may be symmetrical or asymmetrical as in formula (2) or (3): compounds constituted as in formula (4) are tertiary hydrazines, whilst quaternary hydrazines have a structure represented by formula (5).

General methods of preparation.—The primary and secondary hydrazines can be considered as being derived from the primary and secondary amines respectively by the replacement of one of the hydrogen atoms attached to the nitrogen by the primary amino group—

$$RNHH \rightarrow RNH{\cdot}NH_2, \quad RRNH \rightarrow RRN{\cdot}NH_2$$

These compounds are therefore prepared from the primary and secondary amines through the agency of nitrous acid.

Since the primary aromatic amines yield diazonium salts when treated with nitrous acid, these salts are always intermediate products in the formation of the primary aromatic hydrazines and are converted into them by the action of reducing agents. For general purposes this reduction may be effected in one of two ways—

(1) By the reduction of the solution of the diazonium salt by stannous chloride (V. Meyer and Lecco, Ber. 1883, 16, 2976)—

$$C_6H_5{\cdot}N_2Cl+4H=C_6H_5{\cdot}NH{\cdot}NH_2,HCl$$

(2) By treating the diazonium salt with alkali sulphite, in order to prepare the alkali salt of the sulphonic acid, and then by reducing this with zinc dust and acetic acid to form the alkali salt of the hydrazine sulphonic acid thus—

$$C_6H_5{\cdot}N_2SO_3K+2H=C_6H_5{\cdot}NH{\cdot}NH{\cdot}SO_3K$$

Finally, by boiling this salt with hydrochloric acid to convert it into the hydrochloride of the hydrazine and potassium hydrogen sulphate (E. Fischer, Annalen, 1877, 190, 71; Reychler, 1887, 20, 2463)

$$C_6H_5{\cdot}NH{\cdot}NH{\cdot}SO_3K+H_2O+HCl \\ =C_6H_5{\cdot}NH{\cdot}NH_2,HCl+KHSO_4$$

These reactions can only be applied to the aromatic amines because those of the aliphatic series do not form diazonium salts.

Primary aliphatic hydrazines have, however, been prepared by E. Fischer (Ber. 1884, 2841; Annalen, 1877, 199, 281) from the symmetrical dialkyl ureas by transforming them into their nitroso derivatives by the aid of nitrous acid and then by converting the hydrazinureas, formed from these on reduction, into the primary hydrazines by the action of fuming hydrochloric acid.

$$RHN{\cdot}CO{\cdot}NHR+NOOH=RHN{\cdot}CO{\cdot}N(NO)R$$
$$RHN{\cdot}CO{\cdot}N(NO)R+4H \\ =RHN{\cdot}CO{\cdot}N(NH_2)R+H_2O$$
$$RHN{\cdot}CO{\cdot}N(NH_2)R+H_2O \\ =CO_2+(NH_2)NH{\cdot}R+NH{\cdot}R$$

Primary hydrazines of the aromatic series are also formed when certain diazoamino compounds are reduced in alcoholic solution with zinc dust and acetic acid. Thus diazoaminobenzene passes in this manner into phenylhydrazine (E. Fischer, Annalen, 1887, 90, 77).

$$C_6H_5{\cdot}N_2{\cdot}NH(C_6H_5)+4H \\ =C_6H_5{\cdot}NH{\cdot}NH_2+C_6H_5NH_2$$

The secondary hydrazines both of the aromatic and aliphatic series are prepared from the corresponding secondary amines. The amines are converted into their nitroso derivatives by the aid of nitrous acid, which are then transformed into the hydrazines by reduction.

$$R_2NH+NOOH=R_2N{\cdot}NO+H_2O$$
$$R_2N{\cdot}NO+4H=R_2N{\cdot}NH+H_2O$$

Phenylhydrazine $C_6H_5{\cdot}NH{\cdot}NH_2$, the most important member of the hydrazine group, can be prepared by either of the methods mentioned above.

(1) *From aniline by the aid of stannous chloride.* Ten grams of aniline are dissolved in 100 grams of concentrated hydrochloric acid, and the semi-solid mass of aniline hydrochloride is then cooled, externally, by means of ice. A solution of 10 grams of sodium nitrite dissolved in 50 c.c. of water is then gradually added until a test portion diluted with water shows, by means of starch and potassium iodide paper, the presence of excess of nitrous acid. The solution of benzene-diazonium chloride formed in this manner is then treated with a solution of 60 grams of stannous chloride dissolved in 50 c.c. of concentrated hydrochloric acid, the reducing agent being cooled by means of ice and added gradually with constant stirring to the solution of the diazonium salt. After standing for one hour, the phenylhydrazine hydrochloride is filtered at the pump, dissolved in water and converted into the free base by the addition of excess of aqueous caustic potash. The liberated base is extracted with ether, dried by potassium carbonate and purified by distillation under diminished pressure.

(2) *From aniline by the aid of sodium sulphite.* A solution of 50 grams of aniline in 2½ molecules of hydrochloric acid and 300 c.c. of water is diazotised by the addition of the calculated quantity of sodium nitrite solution, and is then mixed with a cold concentrated aqueous solution of 2½ molecules of sodium sulphite. The whole is then gently warmed on the water bath and treated with zinc dust and a little acetic acid until colourless, when it is heated to the boiling-point and filtered, whilst hot, from the unchanged zinc. One-third of its volume of concentrated hydrochloric acid is then added to the hot solution and the phenylhydrazine hydrochloride, which separates on cooling, is removed by filtration and treated in the same manner as in the previous preparation

For the preparation of phenylhydrazine and its derivatives from urea and substituted ureas by the action of alkaline hypobromites, *cp.* Schestakow, D. R. P. 164755; Patentol. 26, 1869.

Tertiary aromatic hydrazines of the general formula $RNH{\cdot}NR_2$ may be prepared by the interaction of β-arylhydroxylamine and magnesium halogen aryl (Busch and Hobein, Ber. 1907, 40, 2099). Thus triphenylhydrazine $C_6H_5NH{\cdot}N(C_6H_5)_2$ is formed when phenylmagnesium bromide reacts with β-phenylhydroxylamine. The corresponding quaternary hydrazine tetraphenylhydrazine

$$(C_6H_5)_2N{\cdot}N(C_6H_5)_2$$

has been prepared by Chattaway and Ingle (Trans. 1895, 67, 1090) by the action of iodine on the sodium compound of diphenylamine, and by Weland and Gambarjan (Ber. 1906, 39, 1501) by the oxidation of diphenylamine.

Certain compounds belonging to the group of the dihydrazines have been prepared by V. Braun (Ber. 1908, 41, 2169; *ibid.* 2604; 1910, 1495), and are recommended as reagents for compounds containing carbonyl oxygen. Thus diphenylmethandimethyldihydrazine

$$[NH_2{\cdot}N(CH_3)C_6H_4]_2CH_2$$

is prepared by condensing methylaniline with formaldehyde to give *p*-dimethyldiaminodiphenylmethane $[HN(CH_3)C_6H_4]_2CH_2$, the nitroso compound of which gives the dihydrazine on reduction with zinc and acetic acid.

Properties and reactions of the hydrazines. The primary aromatic hydrazines are monoacid bases which form well-defined stable salts with both mineral and organic acids. Unlike the corresponding aliphatic primary hydrazines they do not form salts containing two equivalents of a mono-basic acid. The secondary aromatic hydrazines are also mono-acid bases, but their salts are partially decomposed by water. The primary aromatic hydrazines, for example phenylhydrazine, react with metallic sodium forming a sodium compound from which alkyl derivatives can be prepared by the action of alkyl iodides—

$$C_6H_5{\cdot}NNa{\cdot}NH_2 + RI = C_6H_5{\cdot}NR{\cdot}NH_2 + NaI$$

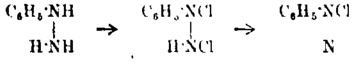
(*cp.* Michaelis, Ber. 1886, 19, 2418; 1887, 20, 43; also Annalen, 1889, 252, 267). The pure sodium compound can be prepared by acting on sodamide with a dilute benzene solution of phenylhydrazine (Titherley, Chem. Soc. Trans. 1897, 71, 461)—

$$NaNH_2 + C_6H_5{\cdot}NH{\cdot}NH_2 = C_6H_5{\cdot}NNa{\cdot}NH_2 + NH_3$$

The corresponding potassium salt may be obtained as large colourless rhombic crystals when phenylhydrazine is treated with a saturated alcoholic solution of potassium hydroxide in the absence of air (Chattaway, Chem. Soc. Trans. 1907, 91, 1326).

The primary hydrazines are readily affected by oxidising agents and are consequently strong reducing agents. Phenylhydrazine reduces Fehling's solution in the cold, even in very dilute solution, a reaction which distinguishes this compound from the secondary base, diphenylhydrazine, which reduces Fehling's solution only on warming. (For the behaviour of phenylhydrazine on oxidation, *cp.* Fischer, Annalen, 1878, 190, 67; 1879, 199, 281; Fischer and Ehrhard, Annalen, 1879, 199, 333; Haller, Ber. 1885, 18, 90; Zincke, *ibid.* 1885, 18, 786; Strache, Monatsh. 1891, 12, 523; 1892, 13, 316; Murster, Ber. 1887, 20, 2633.)

The original statement by Fischer that the oxidation of phenylhydrazine by mercuric oxide leads to a partial production of the diazonium salt has been modified by Chattaway (Chem. Soc. Trans. 1908, 93, 270), who finds that diazonium salts are not produced when the action is carried out in alkaline solution but only in the presence of a large excess of strong acid. Azoimides are formed when alkali is absent and the hydrazines are present in excess. The quantitative conversion of phenylhydrazine into benzenediazonium chloride may be effected by dissolving the hydrazine in glacial acetic acid, cooling the solution to about 15° by the addition of crushed ice and either by passing in a rapid stream of chlorine or (if the diazonium bromide is desired) adding the calculated quantity of bromine dissolved in acetic acid and similarly cooled by ice. The reaction evidently proceeds in accordance with the scheme



$$\begin{array}{c}C_6H_5{\cdot}NH\\ |\\ H{\cdot}NH\end{array} \rightarrow \begin{array}{c}C_6H_5{\cdot}NCl\\ |\\ H{\cdot}NCl\end{array} \rightarrow \begin{array}{c}C_6H_5{\cdot}NCl\\ \\ N\end{array}$$

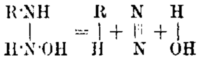
(Chattaway, Chem. Soc. Trans. 1908, 93, 853).

The mechanism of the reaction involved in the oxidation of phenylhydrazine either by oxygen or an oxidising agent, is explained in the following way (Chattaway, Trans. 1908, 93, 270):—

In the first instance, one of the hydrogen atoms of the hydrazino group is attacked and a hydroxyhydrazine is produced

$$RNH{\cdot}NH_2 + O = RNH{\cdot}NH(OH)$$

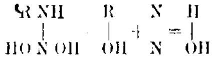
This substance, however, not being stable in the presence of alkali, undergoes disruption in accordance with the scheme



$$\begin{array}{c}R{\cdot}NH\\ |\\ H{\cdot}N{\cdot}OH\end{array} = \begin{array}{c}R\\ |\\ H\end{array} + \begin{array}{c}N\\ |||\\ N\end{array} + \begin{array}{c}H\\ |\\ OH\end{array}$$

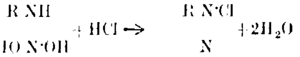
the splitting off of the hydrocarbon and water occurring in either one or two stages.

If, however, a very energetic oxidising agent is used, a certain number of molecules may, before breaking down, undergo a further oxidation thus:—



$$\begin{array}{c}R{\cdot}NH\\ |\\ HO{\cdot}N{\cdot}OH\end{array} \quad \begin{array}{c}R\\ |\\ OH\end{array} + \begin{array}{c}N\\ \\ N\end{array} = \begin{array}{c}H\\ |\\ OH\end{array}$$

yielding a phenol and free nitrogen. In the absence of alkali, which acts as a catalytic agent and much accelerates the decomposition of these hydroxyhydrazines, the introduction of the second hydroxyl group takes place to a much greater extent, and in the presence of strong acid and at a low temperature a diazonium salt is formed, thus—



$$\begin{array}{c}R{\cdot}NH\\ \\ HO{\cdot}N{\cdot}OH\end{array} + HCl \rightarrow \begin{array}{c}R{\cdot}N{\cdot}Cl\\ \\ N\end{array} + 2H_2O$$

The oxidation of phenylhydrazine by basic metallic oxides leads to the formation of the free metal. The following process is recommended for producing a film of metallic copper on glass vessels (Chattaway, Chem. Soc. Trans. 1908, 93, 275; *see* also Proc. Roy. Soc. 1908, A, 80, 88). One part of freshly distilled phenylhydrazine and 2 parts of water are heated until a clear solution is obtained, when it is mixed with about half its bulk of a warm saturated solution of cupric hydroxide in strong ammonia. Nitrogen is freely evolved during the addition, and the cupric hydroxide is reduced to cuprous hydroxide, which remains dissolved in the ammoniacal liquid and does not undergo any immediate further reduction. A hot 10 p.c. solution of potassium hydroxide is then added until a slight permanent precipitate of cuprous hydroxide is produced, and the clear liquid is then cautiously heated in contact with a perfectly clean glass surface. Metallic copper is deposited on it in the form of a thin reflecting coherent lamina. To obtain a film of sufficient thickness, it is best not to pour off the warm reducing fluid but to allow it to remain in contact with the glass until cold. When the liquid is poured off, the film of copper should be well washed with water and afterwards with alcohol and ether. It should then be protected by one or two coats of quickly drying varnish.

When phenylhydrazine is oxidised with copper sulphate or ferric chloride, the parent hydrocarbon is formed and the whole of the nitrogen is eliminated in the free state (Haller, Ber. 1885, 18, 90; Zincke, *ibid.* 786)—

$$C_6H_5{\cdot}NH{\cdot}NH_2 + CuSO_4 + H_2O$$
$$= C_6H_6 + Cu_2O + N_2 + 2H_2SO_4$$

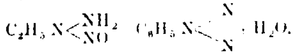
This reaction can be used as a means of estimating phenylhydrazine by measuring the amount of nitrogen evolved (Gallinek and V. v. Richter, Ber. 1885, 18, 3177; Strache, Monatsh. 1891, 12, 524; Strache and Kitt, *ibid.* 1892, 13

310). (For other methods of estimating hydrazines, *cp.* Denigès, Ann. Chim. 1895, [vii.] 6, 381; Causse, Compt. rend. 1897, 125, 712, and Forster, Chem. Soc. Trans. 1898, 74, 792.)

Phenylhydrazine also reacts with hydrogen peroxide, yielding benzene together with some diazobenzeneimide; it moreover acts as a strong reducing agent towards nitro compounds, reducing them to the corresponding amino derivatives (Barr, Ber. 1887, 20, 1498). (For the reduction of nitro compounds, *cp.* also Walter, J. pr. Chem. 1896, [ii.] 53, 433. Reduction of 1:5-dinitroanthraquinone, Schmidt and Gattermann, Ber. 1896, 29, 2941. Reduction of nitro derivatives of phenanthraquinone, Schmidt and Kampf, Ber. 1902, 35, 3124. Reduction of hydroxyazo compounds, Oddo and Puxeddo, Ber. 1905, 38, 2752. Reduction of 5-nitrosalicylic acid, Puxeddo, Gazz. chim. ital. 1906, 36, ii. 87.) The hydrazines resist the action of reducing agents but pass on protracted treatment with zinc dust and hydrochloric acid into aniline and ammonia (E. Fischer, Annalen, 1887, 239, 248) –

$$C_6H_5NH·NH_2 + 2H = C_6H_5·NH_2 + NH_3$$

Primary hydrazines yield with nascent nitrous acid in ice-cold solution unstable nitroso derivatives which pass into diazo-imides and water, when warmed with alkali



$$C_6H_5N<\begin{matrix}NH_2\\NO\end{matrix} = C_6H_5N<\begin{matrix}N\\ \|\\ N\end{matrix} + H_2O.$$

The diazoimide is formed directly if the above reaction is carried out at a higher temperature (E. Fischer, Annalen, 1877, 190, 89, 158, 181). Phenylhydrazine yields *iso*diazobenzene salts with amyl nitrite in the presence of sodium or potassium ethoxide (Stollé, Ber. 1908, 41, 2811). The primary aliphatic hydrazines are hygroscopic liquids readily soluble in water and which possess a smell resembling that of ammonia. The aromatic primary hydrazines are usually solids at the ordinary temperature. They possess a faint aromatic smell and are only sparingly soluble in water.

Phenylhydrazine $C_6H_5·NH·NH_2$ when freshly distilled is a practically colourless, highly refracting oil which distils under diminished pressure without decomposition, or at 240°–241° (780 mm.) with slight evolution of ammonia. When cooled it sets to a mass of tabular monoclinic crystals which melt at 17·5°. According to E. Fischer (Ber. 1908, 41, 73), the melting point of phenylhydrazine is 19·6°, after the substance has been purified first by fractional distillation at 15–20 mm., then by solidification and removal of the liquid portion, an operation repeated four times, then by recrystallisation from anhydrous ether, and finally by distillation under a pressure of 0·5 mm. For ordinary purposes it is sufficient to crystallise the base once or twice from its own volume of pure ether and then distil under a pressure of 10–20 mm. The base should be coloured pale yellow and should dissolve in 10 times its volume of a mixture of 50 p.c. acetic acid (1 part) and water (9 parts). Phenylhydrazine is rather less volatile with steam than aniline and rapidly becomes brown when exposed to the air. It has a sp. gr. of 1·097 at 23°. The base is sparingly soluble in water but forms a hydrate of the formula $2(C_6H_5·NH·NH_2).H_2O$ which melts at 24·1°. It is almost insoluble in concentrated aqueous caustic alkali, but is very readily soluble in certain alkaline salts, such as the alkali salts of the sulphinic and sulphonic acids, soaps, &c. (Otto, Ber. 1894, 27, 2131). For some time it has been prepared on the large scale from diazotised aniline by the sulphite method, and is used commercially for the production of antipyrine, &c., and in the form of its sulphonic acid for the production of the so-called tartrazine colouring matters. Phenylhydrazine is a valuable reagent in organic chemistry, owing to the ease with which it forms crystalline compounds with substances containing carbonyl oxygen. These compounds, which belong to the class of the hydrazones and osazones, are dealt with elsewhere (*see* HYDRAZONES).

When taken internally phenylhydrazine acts as a violent poison, and when brought in contact with the skin causes painful inflammation. Chemists who work much with this substance usually suffer from ill health, of which the most prominent feature is a kind of eczema. It seems to form a definite green compound with the blood to which the name *hæmoverdin* has been given (*cp.* Lewin, Compt. rend. 1901, 133, 599; Zeit. Biol. 1901, 42, 107).

Of the salts of phenylhydrazine, the *hydrochloride* $C_6H_5·NH·NH_2.HCl$ is the most important. It crystallises as colourless glistening leaflets which dissolve readily in hot water but separate from the solution on cooling. It can be recrystallised from alcohol and by careful heating can be sublimed unchanged. Other aromatic hydrazines of importance are:

Diphenylhydrazine $(C_6H_5)_2N·NH_2$. This compound is produced by the reduction of nitrosodiphenylamine $(C_6H_5)_2N·NO$, which is obtained from diphenylamine $(C_6H_5)_2NH$ by the action of nitrous acid (E. Fischer, Annalen, 1877, 190, 174; Stahel, *ibid.* 1890, 258, 242; Overton, Ber. 1893, 26, 19). It forms colourless plates which melt at 34·5°, and is partially decomposed on distillation under diminished pressure. The hydrazine yields well-defined crystalline compounds with sugars and can be used for the quantitative estimation of arabinose (Neuberg and Wohlgemuth, Ber. 1894, 27, 3106).

Methylphenylhydrazine $C_6H_5(CH_3)N·NH_2$ may be prepared either by the reduction of the nitroso compound $C_6H_5(CH_3)N·NO$ (E. Fischer, Annalen, 1877, 190, 150), or by the alkylation of sodium phenylhydrazine by means of methyl iodide (A. Michaelis, Ber. 1886, 19, 2450; Phillips, *ibid.* 1887, 20, 2485). It is a colourless liquid, boiling with slight decomposition and evolution of ammonia at 227° (745 mm.); under a pressure of 75 mm. it boils without decomposition at 131°. Methylphenylhydrazine is a valuable reagent for the isolation of certain ketoses (Neuberg, Ber. 1902, 35, 959).

Phenylbenzylhydrazine

$$C_6H_5(CH_2·C_6H_5)N·NH_2$$

(Ofner, Monatsh. 1904, 25, 593) is prepared by the direct action of benzyl chloride on phenylhydrazine and is a colourless liquid boiling at 216°–218° at 38 mm. It is a useful reagent for the isolation of the sugars, as the hydrazones formed from it are less soluble and more easily produced than those from simpler hydrazines (*cp.* Ruff and Ollendorf, Ber. 1899, 32, 3255; Lobry de Bruyn, Rec. trav. chim. 15, 97, 227).

p-**Bromophenylhydrazine** $H_2N{\cdot}NH{\cdot}C_6H_4Br$ may be prepared by brominating phenylhydrazine hydrochloride in the presence of a large excess of strong hydrochloric acid (Neufeld, Annalen, 1888, 248, 94; L. Michaelis, Ber. 1893, 26, 2191). It crystallises from hot water as long needles which melt at 107° and is a useful reagent for the characterisation of sugars. It has been used for the preparation of hydrazones from certain naturally occurring ketones, as for example camphor (Tiemann and Kruger, Ber 1895, 28, 1756; Tiemann, *ibid.* 2191).

Phenylhydrazine-*p*-sulphonic acid

$$C_6H_4(SO_3H)NH{\cdot}NH_2$$

is of historical interest as being the first derivative of hydrazine to be prepared, and was obtained from diazotised *p*-amidobenzenesulphonic acid by reduction with sodium hydrogen sulphite (Strecker and Romer, Ber. 1871, 4, 784; Romer, Zeitsch Chem 1871, 482). It may be prepared by the direct sulphonation of phenylhydrazine and when pure crystallises as glistening needles containing ½ a molecule of water of crystallisation. It is prepared on the large scale from *p*-sulphanilic acid by diazotisation and reduction with sodium sulphite, and is used for the production of the tartrazine colouring matters (*q.v.*).

p-**Nitrophenylhydrazine** $C_6H_4(NO_2)NH{\cdot}NH_2$. This substance is recommended by Bamberger (Ber. 1899, 32, 1806) for the investigation of aldehydes and ketones as being more stable than *p*-bromophenylhydrazine It is prepared from the sodium salt of *p*-nitrophenylhydrazinesulphonic acid by the action of concentrated hydrochloric acid (Purgotti, Ber. 1892, 25 119; Bamberger and Sternitzki, *ibid* 26, 1306), and also by boiling the potassium salt of *p*-nitrophenylhydrazinedisulphonic acid with dilute hydrochloric acid (Hantzsch and Borghaus, Ber 1897, 30, 91). It may also be prepared from *p*-nitraniline by diazotisation and reduction. The base forms orange red leaflets and needles from hot alcohol, which melt with decomposition at 157°. (For the use of this base in the preparation of hydrazones of the aldehydes and ketones, *cp.* Bamberger, Ber. 1899, 32, 1806; Hyde, *ibid.* 1810.)

The naphthylhydrazines. Both the *α*- and *β*-naphthylhydrazines can be used for the preparation of hydrazones from compounds containing carbonyl oxygen, but the *β*- compound is especially recommended by Hilger and Rothenfusser (Ber. 1902, 35, 2627) for the isolation of numerous sugars. The two bases are prepared in a similar manner from the corresponding diazonaphthalenes on reduction with stannous chloride, or by heating the naphthol with hydrazine hydrate at 160° (Hoffmann, Ber. 1898, 31, 2909). *α*-Naphthylhydrazine forms leaflets from water which melt at 116°–117° and boil almost without decomposition at 203° (20 mm.) (Knorr, Ber. 1884, 17, 551). *β*-Naphthylhydrazine forms glistening leaflets from water which melt at 124°–125° (*cp.* also Franzen, Ber. 1905, 38, 266).

HYDRAZINE AND SOME OF ITS DERIVATIVES USED AS REAGENTS FOR THE ISOLATION OF ALDEHYDES AND KETONES.

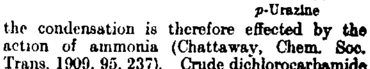
Hydrazine $H_2N{\cdot}NH_2$. This substance was first prepared by Curtius by the action of hot dilute acids on triazoacetic acid (Ber. 1887, 20, 1632). It has since been obtained by other methods of which the more important are (1) from aminoguanidine $H_2N{\cdot}C(NH)NH{\cdot}NH_2$ on treatment with caustic alkali (Thiele, Annalen, 270, 1). (2) From sodium hypochlorite and ammonia (Raschig, D. R. PP. 192783, 198307; Chem. Zentr. 1908, i. 427, 1957). This process consists in heating the hypochlorite solution with excess of ammonia, when the monochloramine first formed reacts with the ammonia to form hydrazine: on boiling off the excess of ammonia and neutralising with sulphuric acid the sparingly soluble hydrazine sulphate crystallises out.

$$(1)\ NH_3+NaOCl = NH_2Cl+NaOH$$
$$(2)\ 3NH_2Cl+2NH_3 = N_2+3NH_4Cl$$
$$(3)\ NH_2Cl+NH_3 = \underset{\text{hydrazine hydrochloride.}}{N_2H_4HCl}$$

By adding cane sugar, dextrin, starch, glycerol, gelatin, albumin, &c., to the solution so as to increase its viscosity reaction (2) is retarded and the yield of the hydrazine salt according to equation (3) is greatly increased (Eng. Pat. 39, 1908) (3) From dichlorocarbamide (Chattaway, Chem. Soc. Trans 1909, 95, 237). The last-named preparation is carried out in the following way:—

Dichlorocarbamide $NHCl{\cdot}CO{\cdot}NHCl$ (Chattaway, Chem. Soc Trans 1909, 95, 465). Six grams of carbamide are dissolved in 50 c.c. of distilled water and 10 grams of finely divided zinc oxide are added. The mixture is cooled to about −5° in a freezing mixture and a rapid stream of chlorine passed through the liquid. If the operation is carried out in a small flask, and this is well shaken in the freezing mixture during the passage of the gas, the temperature does not rise above zero. The zinc oxide quickly dissolves and a clear liquid results, from which in a short time crystals of dichlorocarbamide begin to separate. When the liquid has become a thick pulp from the separated solid and crystals no longer appear to separate, the dichlorocarbamide is rapidly collected at the pump, washed twice with 5 c.c. of ice-cold distilled water and then several times with chloroform. The yield is 77·5 p.c. of the theory.

p-**Urazine.** This substance is formed by the elimination of hydrogen chloride from two molecules of monochlorocarbamide, which may be regarded as the initial product formed by the action of ammonia on dichlorocarbamide—



$$\mathrm{CO}{<}\begin{smallmatrix}\mathrm{NHCl}\\ \mathrm{NH_2}\end{smallmatrix} + \begin{smallmatrix}\mathrm{H_2N}\\ \mathrm{ClHN}\end{smallmatrix}{>}\mathrm{CO} \rightarrow \mathrm{CO}{<}\begin{smallmatrix}\mathrm{NH-NH}\\ \mathrm{NH-NH}\end{smallmatrix}{>}\mathrm{CO}$$

p-Urazine

the condensation is therefore effected by the action of ammonia (Chattaway, Chem. Soc. Trans. 1909, 95, 237). Crude dichlorocarbamide free from all adhering mother-liquor is dissolved in from 10 to 20 times its weight of water and rapidly added to excess of strong ammonia, the mixture being thoroughly stirred. A vigorous evolution of nitrogen takes place and a white crystalline powder separates; a little more crystallises out on keeping, and a still further small quantity on evaporating the mother-liquor after neutralising with hydrochloric acid.

Hydrazine sulphate. When *p*-urazine is mixed with about 5 times its weight of concentrated sulphuric acid and warmed to about 80°, it dissolves apparently without change; on heating the solution to about 95–100°, hydrolysis slowly takes place with evolution of carbon dioxide. On raising the temperature still higher, the rate of evolution of carbon dioxide increases, until, at about 120°–130°, it is very rapidly liberated; at this temperature, hydrolysis is soon complete and a clear colourless liquid is obtained which deposits crystals of hydrazine sulphate on cooling. It is best, however, to add to the cooled liquor its own bulk of water, when pure hydrazine sulphate at once separates as a white crystalline powder.

Free hydrazine has been prepared by Lobry de Bruyn (Ber. 1895, 27, 3085) by the action of sodium methoxide in methyl alcohol on hydrazine hydrochloride, and also by heating the hydrate N_2H_4,H_2O with barium oxide at 100°. It is a very stable liquid which boils without decomposition at 113·5° (761 mm.), and at 56° (71 mm.). It solidifies when cooled below 0°, and then melts at 1·4°. It has a sp. gr. of 1·003 at 23° (*cp.* Rasching, Ber. 1910, 43, 1927).

Hydrazine hydrate $N_2H_4.H_2O$ is the form in which hydrazine is liberated from its salts by the action of aqueous alkalis. It is a strongly refracting, almost odourless liquid, which boils without decomposition at 118·5° (739·5 mm.) and solidifies when placed in a mixture of solid carbon dioxide and ether, but melts again below −40°. It is advisable when preparing this substance to employ a silver retort and to avoid the use of rubber connections, as the hydrate, when hot, attacks glass strongly and quickly destroys cork and rubber.

Semicarbazide $H_2N{\cdot}CO{\cdot}NH{\cdot}NH_2$. This substance was first used for the preparation of derivatives of ketones by Baeyer acting on the suggestion of Thiele (Ber. 1894, 27, 1918), the compound having been prepared earlier in the year by Thiele and Stange (Ber. 1894, 27, 31; Annalen, 1894, 283, 19), who obtained it by the action of potassium cyanate on hydrazine sulphate, and by Curtius and Heidenreich (Ber. 1894, 27, 56), who prepared it by the interaction of hydrazine hydrate and urea. Semicarbazide may be conveniently prepared in the following way: 225 grams of nitrourea in 1700 c.c. of concentrated hydrochloric acid are mixed at 0° with excess of zinc dust and are then left for a short time after all action has subsided. The filtered solution, after being saturated with sodium chloride, is treated with 200 grams of sodium acetate and 100 grams of acetone. The acetonesemicarbazone zinc chloride, which separates after some time, is washed with salt solution and decomposed by strong ammonia (350 c.c. to 200 grams of the compound) (Thiele and Heuser, Annalen, 1895, 288, 312).

Semicarbazide crystallises from absolute alcohol as prisms which melt at 96°. It readily reacts with substances containing carbonyl oxygen, in accordance with the scheme

$$H_2N{\cdot}CO{\cdot}NH{\cdot}NH_2+OCR_2 = H_2N{\cdot}CO{\cdot}NH{\cdot}N:CR_2+H_2O$$

forming semicarbazones which possess the advantage of being readily decomposed into their components on treatment with dilute acids. The method recommended by Baeyer (Ber. 1894, 27, 1918) for the preparation of a semicarbazone is as follows:

Semicarbazide hydrochloride is dissolved in a little water and the requisite amount of alcoholic potassium acetate together with the ketone are added, as well as sufficient alcohol and water to effect complete solution. The length of time required for the reaction depends on the nature of the ketone and varies from a few minutes to 4–5 days; it is finished when the addition of water precipitates a crystalline solid. Semicarbazide is usually met with in the form of its hydrochloride. The free base slowly alters on keeping.

Thiosemicarbazide $NH_2{\cdot}CS{\cdot}NH{\cdot}NH_2$. This substance, like semicarbazide, reacts with compounds containing carbonyl oxygen in accordance with the equation—

$$H_2N{\cdot}CS{\cdot}NH{\cdot}NH_2+OCR_2 = H_2N{\cdot}CS{\cdot}NH{\cdot}N:CR_2+H_2O$$

forming thiosemicarbazones, which possess the property of forming insoluble salts with the heavy metals from which the ketone or aldehyde can be readily regenerated (Neuberg and Neimann, Ber. 1902, 2049).

The base can be prepared from hydrazine sulphate in the following manner (Freund and Schander, Ber. 1896, 29, 2501; Freund and Imgart, *ibid.* 1895, 28, 948): 50 grams of hydrazine sulphate and 27 grams of anhydrous potassium carbonate are dissolved in 200 c.c. of water and mixed with 40 grams potassium thiocyanate. The mixture is boiled for some minutes and is then treated with 200–300 c.c. of hot alcohol and filtered. The filtrate is freed from alcohol by vigorously boiling and, when cooled, deposits long needles of the base which melt at 181°.

Semioxamazide $H_2N{\cdot}CO{\cdot}CO{\cdot}NH{\cdot}NH_2$ (Kerp and Unger, Ber. 1897, 30, 586). This substance may be prepared by gently heating oxamethane with an alcoholic solution of hydrazine for a short time on the water bath. It crystallises in slender lustrous leaflets which melt and decompose at 220°–221°. Semioxamazones are produced in quantitative yield from aldehydes, but the ketones react in a less general manner and seem to require special conditions for their formation.

Aminoguanidine $H_2N{\cdot}C(NH)NH{\cdot}NH_2$ is prepared from nitroguanidine on reduction (Thiele, Annalen, 270, 23; D. R. P. 59241; Frdl. iii. 16), and from cyanamide, hydrazine hydrochloride and alcohol (Pellizari and Cuneo, Gazz. chim. ital. 1894, 24, 453). The hydrochloride forms long prisms from dilute alcohol which melt at 163°.

The base is recommended by Baeyer (Ber. 1894, 27, 1918) for the preparation of derivatives of ketones, the following method being used.

Aminoguanidine hydrochloride is dissolved in a little water containing a trace of hydrochloric acid and is then mixed with the ketone together with sufficient alcohol to effect solution. The reaction is finished after warming for a short time on the water bath, when water and caustic potash solution are added and the base is extracted by ether. The oil which remains after evaporating the ether is suspended in hot water and heated with an aqueous solution of picric acid. The picrate separates as a crystalline precipitate which is recrystallised either from dilute or absolute alcohol, according to its solubility. J. F. T.

HYDRAZOBENZENE Prepared by reducing nitrobenzene in hot alkaline solution with zinc dust or iron in presence of alcohol or solvent naphtha. May also be obtained by electrolysis; m.p. 127 (Darmstadter, D. R. P 181116, 189312)

HYDRAZONES Substances containing the complex $>\mathrm{N}\cdot\mathrm{NH_2}$ react with those compounds which have in their molecule an oxygen atom doubly bound to carbon, forming condensation products in accordance with the general equation

$$>\mathrm{C}:\mathrm{O}+\mathrm{H_2N}\cdot\mathrm{N}< \rightarrow\ >\mathrm{C}:\mathrm{N}\cdot\mathrm{N}<+\mathrm{H_2O}.$$

Such condensation products are termed hydrazones. Only the carbonyl compounds which belong to the groups of the aldehydes and ketones react in this manner; the carboxylic acids containing the group COOH do not react as if they contained carbonyl oxygen, but give hydrazides in accordance with the scheme

$$\mathrm{R}\cdot\mathrm{COOH}+\mathrm{H_2N}\cdot\mathrm{N}< \rightarrow \mathrm{R}\cdot\mathrm{CO}\cdot\mathrm{NH}\cdot\mathrm{N}<+\mathrm{H_2O}.$$

One or more carbonyl- groups present in the compound may enter into combination with the hydrazine residue, forming for example, in the case of the dicarbonyl derivatives dihydrazones, thus

$$\begin{array}{l}-\mathrm{CO}\quad \mathrm{C}:\mathrm{N}\cdot\mathrm{N}<\\ -\mathrm{CO}\quad \mathrm{C}:\mathrm{N}\cdot\mathrm{N}<\end{array}$$

Those dihydrazones, which are derived from dicarbonyl compounds having the two carbonyl-groups on contiguous carbon atoms, are termed osazones. Thus in the case of the two compounds formed from glyoxal CHO·CHO and phenylhydrazine

$$\begin{array}{l}\mathrm{CHO}\\ |\\ \mathrm{CH}:\mathrm{N}\cdot\mathrm{NHC_6H_5}\end{array}\qquad \text{is glyoxalphenylhydrazone,}$$

$$\begin{array}{l}\mathrm{CH}:\mathrm{N}\cdot\mathrm{NHC_6H_5}\\ \\ \mathrm{CH}:\mathrm{N}\cdot\mathrm{NHC_6H_5}\end{array}\qquad \text{is glyoxalphenylosazone}$$

(Fischer, Ber. 1888, 21, 985).

Phenylhydrazine $\mathrm{C_6H_5}\cdot\mathrm{NH}\cdot\mathrm{NH_2}$ was the first member of the class of the hydrazines to be applied to the characterisation and isolation of the carbonyl compounds (comp. E. Fischer, Ber. 1884, 17, 572), but since that time the reaction has been shown to be a general one for all derivatives of hydrazine having a primary amino group intact.

Hydrazine $\mathrm{H_2N}\cdot\mathrm{NH_2}$ itself reacts with aldehydes and ketones, as Curtius has shown, forming either hydrazones of the type

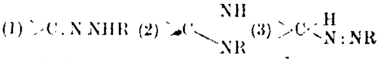
$$\mathrm{R}\cdot\mathrm{CH}:\mathrm{N}\cdot\mathrm{NH_2}$$

(or $\mathrm{RRC}:\mathrm{N}\cdot\mathrm{NH_2}$), in which one molecule of the carbonyl compound reacts, or azines of the formula $\mathrm{R}\cdot\mathrm{CH}:\mathrm{N}\cdot\mathrm{N}:\mathrm{CHR}$ (or $\mathrm{RRC}:\mathrm{N}\cdot\mathrm{N}\cdot\mathrm{CRR}$), in which two molecules of the carbonyl derivative take part. The azines from the aldehydes are known as aldazines, those from the ketones as ketazines. In the aliphatic series, the aldehydes pass directly into the aldazines when treated with hydrazine, whilst the hydrazones, $\mathrm{RRC}:\mathrm{N}\cdot\mathrm{NH_2}$, which can be isolated from the product of the interaction of ketones and hydrazine, readily pass into the ketazine and hydrazine in accordance with the equation

$$2(\mathrm{R_2C}:\mathrm{N}\cdot\mathrm{NH_2}) \rightarrow \mathrm{R_2C}:\mathrm{N}\cdot\mathrm{N}\cdot\mathrm{R_2}+\mathrm{H_2N}\cdot\mathrm{NH_2}$$

It is apparent that azine formation in the manner described above cannot occur with the substituted derivatives of hydrazine of the general formulæ $\mathrm{RNH}\cdot\mathrm{NH_2}$ and $\mathrm{R_2N}\cdot\mathrm{NH_2}$, and it is therefore compounds of this type which are of such great importance as reagents for the preparation of the hydrazones, osazones, and semicarbazones

Constitution of the hydrazones. The constitution of the hydrazones formed from carbonyl compounds by the action of secondary asymmetric hydrazines $\mathrm{R_2N}\cdot\mathrm{NH_2}$, admits of only one formula, namely, $\mathrm{R_2N}\cdot\mathrm{N}:\mathrm{CR_2}$; but the hydrazones formed from the primary hydrazines may conceivably be constituted in accordance with one or other of the three forms



$$(1)\ >\mathrm{C}:\mathrm{N}\cdot\mathrm{NHR}\quad (2)\ >\mathrm{C}<\begin{array}{l}\mathrm{NH}\\ |\\ \mathrm{NR}\end{array}\quad (3)\ >\mathrm{C}<\begin{array}{l}\mathrm{H}\\ \mathrm{N}:\mathrm{NR}\end{array}$$

Of these, formula (2) may be discarded, because the same compound is formed by the interaction of benzaldehyde and phenylethylhydrazine

$$\mathrm{C_6H_5}\cdot\mathrm{CHO}+\mathrm{H_2N}\cdot\mathrm{N(C_2H_5)C_6H_5} = \mathrm{C_6H_5}\cdot\mathrm{CH}:\mathrm{N}\cdot\mathrm{N(C_2H_5)C_6H_5}$$

as by the ethylation, by means of sodium ethoxide and ethyl iodide, of the hydrazone formed by the condensation of benzaldehyde and phenylhydrazine

$$\mathrm{C_6H_5}\cdot\mathrm{CHO}+\mathrm{H_2N}\cdot\mathrm{NH}\cdot\mathrm{C_6H_5} = \mathrm{C_6H_5}\cdot\mathrm{CH}:\mathrm{N}\cdot\mathrm{NH}\cdot\mathrm{C_6H_5}$$

$$\mathrm{C_6H_5}\cdot\mathrm{CH}:\mathrm{N}\cdot\mathrm{NH}\cdot\mathrm{C_6H_5}+\mathrm{NaO}\cdot\mathrm{C_2H_5} = \mathrm{C_6H_5}\cdot\mathrm{CH}:\mathrm{N}\cdot\mathrm{NNa}\cdot\mathrm{C_6H_5}+\mathrm{HO}\cdot\mathrm{C_2H_5}$$

$$\mathrm{C_6H_5}\cdot\mathrm{CH}:\mathrm{N}\cdot\mathrm{NNa}\cdot\mathrm{C_6H_5}+\mathrm{C_2H_5I} = \mathrm{C_6H_5}\cdot\mathrm{CH}:\mathrm{N}\cdot\mathrm{N(C_2H_5)C_6H_5}+\mathrm{NaI}$$

The azo formula (3) would appear, at first sight, to be untenable, because the hydrazone prepared from phenylhydrazine and acetaldehyde is different from ethaneazobenzene

$$\mathrm{CH_3}\cdot\mathrm{CH_2}\cdot\mathrm{N}:\mathrm{N}\cdot\mathrm{C_6H_5}$$

which is prepared by the oxidation of ethanehydrazobenzene. It has been shown, however, that there is an intimate connection between these two substances, and that the change

$$\mathrm{C_6H_5}\cdot\mathrm{N}:\mathrm{N}\cdot\mathrm{C_2H_5} \rightarrow \mathrm{C_6H_5}\cdot\mathrm{NH}\cdot\mathrm{N}:\mathrm{CHCH_3}$$

is readily effected by mineral acids (Fischer, Annalen, 1879, 199, 328; Ber. 1896, 29, 703), or by sodium ethoxide (Bamberger, Ber. 1903, 36, 56); whereas the reverse change

$$\mathrm{C_6H_5}\cdot\mathrm{NH}\cdot\mathrm{N}:\mathrm{CHCH_3} \rightarrow \mathrm{C_6H_5}\cdot\mathrm{N}:\mathrm{N}\cdot\mathrm{CH_2CH_3}$$

is effected by the action of light (Chattaway, Chem. Soc Trans. 1906, 89, 462). The question as to the azo or hydrazone structure of these compounds has given rise to a great deal of controversy, and is even at the present time not definitely settled. The discussion may be said to have arisen owing to the discovery made by Japp and Klingemann (Ber. 1887, 20, 3284, 3398), that the hydrazone of pyruvic acid

$$\mathrm{C_6H_5NH}\cdot\mathrm{N}:\mathrm{C(CH_3)CO_2H}$$

was identical with benzene-α-azopropionic acid $C_6H_5N : N\cdot CH(CH_3)CO_2H$. R. Meyer (Ber. 1888, 21, 118) also showed that the dicarboxylic acid obtained by the hydrolysis of the ethyl salt which is formed by the interaction of benzenediazonium chloride and ethyl malonate, thus:

$$C_6H_5\cdot N_2Cl+CH_2(CO_2R)_2 = C_6H_5\cdot N : N\cdot CH(CO_2R)_2+HCl$$

$$C_6H_5\cdot N : N\cdot CH(CO_2R)_2+2H_2O = C_6H_5\cdot N : N\cdot CH(CO_2H)_2+2R\cdot OH$$

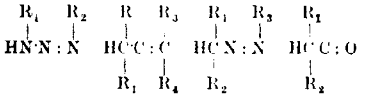
was identical with the compound prepared by the condensation of mesoxalic acid and phenylhydrazine, thus:

$$C_6H_5\cdot NH\cdot NH_2+CO(CO_2H)_2 = C_6H_5\cdot NH\cdot N : C(CO_2H)_2+H_2O$$

That is to say, the question arose as to whether these compounds were true hydrazones having the structure $R\cdot NH\cdot N : C<$ or whether they were azo compounds having the structure $R\cdot N : N\cdot CH<$.

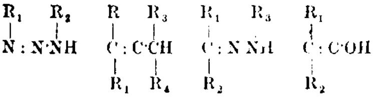
Since that time many other instances of the same kind as that recorded by these chemists have been investigated, and repeated attempts have been made to establish either one or other of these constitutional formulæ for the hydrazones (R. Meyer, Ber. 1891, 24, 1241; Japp and Klingemann, Annalen, 1888, 247, 190; V. Meyer, Ber. 1888, 21, 11; Haller, Compt. rend. 1888, 106, 1173; Beyer and Claisen, Ber. 1892, 25, 746; v. Pechmann, Ber. 1892, 25, 3190; Bamberger and Wheelwright, *ibid.* 1892, 25, 3201; Bamberger, *ibid.* 1894, 27, 2591).

Much of the evidence falls under the head of the constitution of the azo compounds, and the article under this heading should be consulted for further information; but it is evident that much still remains to be learnt regarding the conditions controlling the tendency of a hydrogen atom attached to the terminal atom of any system such as



$$\begin{array}{ccc} R_1 & & R_2 \\ | & & | \\ HN & \cdot N : & N \end{array} \qquad \begin{array}{ccc} R & & R_3 \\ | & & | \\ HC & \cdot C : & C \\ | & & | \\ R_1 & & R_4 \end{array} \qquad \begin{array}{ccc} R_1 & & R_3 \\ | & & | \\ HC & \cdot N : & N \\ | & & \\ R_2 & & \end{array} \qquad \begin{array}{cc} R_1 & \\ | & \\ HC & \cdot C : O \\ | & \\ R_2 & \end{array}$$

to pass to the other terminal atom with a consequent shifting of the double bond, thus:



$$\begin{array}{ccc} R_1 & & R_2 \\ | & & | \\ N & : N\cdot & NH \end{array} \qquad \begin{array}{ccc} R & & R_3 \\ | & & | \\ C & : C\cdot & CH \\ | & & | \\ R_1 & & R_4 \end{array} \qquad \begin{array}{ccc} R_1 & & R_3 \\ | & & | \\ C & : N\cdot & NH \\ | & & \\ R_2 & & \end{array} \qquad \begin{array}{cc} R_1 & \\ | & \\ C & : C\cdot OH \\ | & \\ R_2 & \end{array}$$

The evidence at present available seems to show that the hydrogen atom in compounds of this type may assume either one or other of these positions, in which case definite compounds are formed, having, as in the case under discussion, either the azo or hydrazone form: on the other hand, there may be tautomerism between the two forms, in which case the hydrogen atom acts as if it vibrated between the two terminal atoms of the system (*cf.* Bulow and Hopfner, Ber. 1901, 34, 71; Bülow and Hailer, *ibid.* 1902, 35, 915). There is, however, little doubt that in the majority of cases the compounds formed from benzenediazonium chloride and substances of the type of ethyl malonate as well as those produced by the action of phenylhydrazine on carbonyl compounds have the hydrazone structure.

The formation of phenylhydrazones. As a rule, phenylhydrazine readily reacts with ketones and aldehydes, yielding phenylhydrazones, which are crystalline and of definite melting-point. The following method generally gives the phenylhydrazone in a pure condition. Phenylhydrazine is dissolved in 50 p.c. aqueous acetic acid and diluted with three times its volume of water. The carbonyl compound diluted when necessary by a suitable solvent is then added and the whole is warmed. The phenylhydrazone then separates either in the crystalline condition or as an oil which usually crystallises when scratched with a glass rod.

Derivatives of phenylhydrazine, such as phenylhydrazine-*p*-sulphonic acid

$$C_6H_4(SO_3H)NH\cdot NH_2$$

p-nitrophenylhydrazine $C_6H_4(NO_2)NH\cdot NH_2$ or *p*-bromophenylhydrazine

$$C_6H_4(Br)NH\cdot NH_2$$

may be used for the production of hydrazones; moreover other hydrazines, such as β-naphthylhydrazine $C_{10}H_7\cdot NH\cdot NH_2$, methylphenylhydrazine $C_6H_5(CH_3)N\cdot NH_2$, *asym*-diphenylhydrazine $(C_6H_5)_2N\cdot NH_2$, and benzylphenylhydrazine $C_6H_5\cdot CH_2(C_6H_5)N\cdot NH_2$ are often used for this purpose (*cp.* HYDRAZINES).

Reaction of the hydrazones. When warmed with mineral acids, the hydrazones are more or less readily hydrolysed into the carbonyl compound and the hydrazine. This reaction proceeds, however, much more readily when the hydrazone is warmed with an aqueous solution of pyruvic acid, when the following reaction often occurs (Fischer and Ach, Annalen, 1889, 253, 57):—

$$R_2C : N\cdot NH\cdot C_6H_5+CH_3\cdot CO\cdot CO_2H = R_2CO+CH_3\cdot C(:N\cdot NH\cdot C_6H_5)CO_2H$$

The hydrazones of the aliphatic aldehydes and ketones form addition products with hydrocyanic acid, yielding nitriles in accordance with the equation

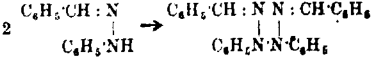
$$C_6H_5\cdot NH\cdot N : CR_2+HCN = C_6H_5\cdot NH\cdot NH\cdot C(CN)\cdot R_2$$

(*cp.* V. Miller and Plöchl, Ber. 1892, 25, 2023).

Hydrazones when reduced break at the point of union of the two nitrogen atoms and pass into amines. This method has been made use of by Tafel (Ber. 1886, 19, 1924; 1889, 22, 1854) for the formation of primary amines from aldehydes and ketones. Thus the hydrazone of acetaldehyde yields in this manner a mixture of aniline and ethylamine

$$CH_3\cdot CH : N\cdot NH\cdot C_6H_5+4H = CH_3\cdot CH_2NH_2+C_6H_5NH_2$$

When oxidised by amyl nitrite, hydrazones are converted into hydrotetrazines (V. Pechmann, Ber. 1893, 26, 1045).

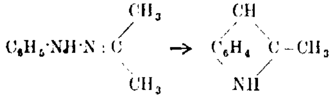


$$2\begin{array}{c} C_6H_5\cdot CH : N \\ | \\ C_6H_5\cdot NH \end{array} \rightarrow \begin{array}{c} C_6H_5\cdot CH : N\ \ N : CH\cdot C_6H_5 \\ |\ \ | \\ C_6H_5N\cdot N\cdot C_6H_5 \end{array}$$

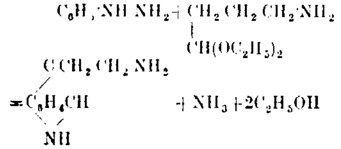
These compounds dissolve in concentrated sulphuric acid, forming intensely coloured solutions. It is probable that Bülow's reaction for hydrazides and hydrazones, which depends on the formation of a coloured solution, when the hydrazone, dissolved in concentrated sulphuric acid, is treated with a drop of ferric chloride solution, is due to the production of the hydrotetrazine.

The action of zinc chloride on hydrazones causes the elimination of ammonia and leads to the formation of derivatives of indole (E. Fischer and Hess, Ber. 1884, 17, 559; E. Fischer, *ibid* 1886, 19, 1563; Annalen, 1886, 236, 116; Brunner, Monatsh. 1895, 16, 183, 849).

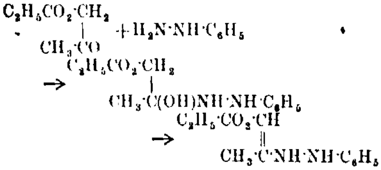
The reaction may be expressed by the following general equation, but is difficult to follow by means of structural formulæ:—



This reaction has been made use of by Ewins (Chem Soc. Trans. 1911, 99, 270) for the preparation of 3-β-aminoethylindole, thus—

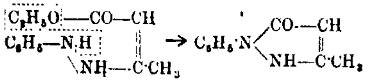


This compound was found to be identical with the base obtained by the action of putrefactive bacteria on tryptophan It will be noticed that, owing to the unstable character of the aldehyde, it could not be used in the free state for the production of the hydrazone and that the acetal derivative was used in its place. Hydrazones which are formed from β-ketonic ethyl salts pass, when heated, into alcohol and a derivative of pyrazolone. Thus the phenylhydrazone of ethyl acetoacetate, which is a colourless crystalline substance and is therefore probably ethyl benzenehydrazocrotonate formed in accordance with the equation



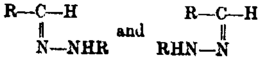
$$\begin{array}{l} C_2H_5CO_2{\cdot}CH_2 \\ \quad | \qquad + H_2N{\cdot}NH{\cdot}C_6H_5 \\ CH_3{\cdot}CO \end{array} \rightarrow \begin{array}{l} C_2H_5CO_2{\cdot}CH_2 \\ \quad | \\ CH_3{\cdot}C(OH)NH{\cdot}NH{\cdot}C_6H_5 \end{array} \rightarrow \begin{array}{l} C_2H_5{\cdot}CO_2{\cdot}CH \\ \quad \| \\ CH_3{\cdot}C{\cdot}NH{\cdot}NH{\cdot}C_6H_5 \end{array}$$

passes when heated at 200° under diminished pressure into phenylmethylpyrazolone



In many cases the formation of the pyrazolone derivative takes place immediately without the intermediate formation of the hydrazone.

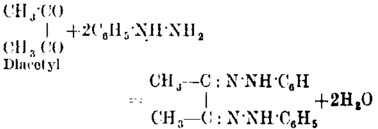
Stereoisomerism, in accordance with the Hantzsch-Werner hypothesis, has been observed among the hydrazones, and in certain instances the two forms



$$\begin{array}{l} R{-}C{-}H \\ \quad \| \\ \quad N{-}NHR \end{array} \quad \text{and} \quad \begin{array}{r} R{-}C{-}H \\ \| \quad \\ RHN{-}N \quad \end{array}$$

have been isolated (*cp.* E. Fischer, Ber. 1884, 17, 575; Biltz, *ibid.* 1894, 2288; Hantzsch and Hornbostel, *ibid.* 1897, 30, 3003; Bamberger and Schmidt, *ibid.* 1901, 34, 2001).

As already mentioned, the name 'osazone' denotes a compound containing in its molecule two hydrazine residues, R—NH—N=, attached to two contiguous carbon atoms. E. Fischer (Ber. 1884, 17, 579) obtained from carbohydrates a series of characteristic compounds formed by the introduction of two phenylhydrazone groups into the molecule of a carbohydrate. The compound from dextrose was termed 'phenyl glucosazone'; that from galactose 'phenylgalactosazone,' and so on. Later, when it was found that in these compounds the two phenylhydrazine residues were in contiguous positions, the name 'osazone' was applied to all compounds containing this particular grouping (E. Fischer, Ber. 1888, 21, 985). Osazones are formed by the action of two molecules of phenylhydrazine on α-dicarbonyl compounds, namely, such as contain the group CO·CO;



$$\begin{array}{l} CH_3{\cdot}CO \\ \quad | \quad + 2C_6H_5{\cdot}NH{\cdot}NH_2 \\ CH_3{\cdot}CO \\ \text{Diacetyl} \end{array} = \begin{array}{l} CH_3{-}C : N{\cdot}NH{\cdot}C_6H \\ \qquad | \\ CH_3{-}C : N{\cdot}NH{\cdot}C_6H_5 \end{array} + 2H_2O$$

Diacetylphenylosazone.

The yellow colouring matters known as 'tartrazines' are derived from osazones, formed in this way from dihydroxytartaric acid.

Osazones are also formed by the action of phenylhydrazine on compounds containing the group —CH(OH)·CO—, thus on α-keto-alcohols and α-aldehydo-alcohols; and it is the members of the carbohydrate family belonging to these classes which yield ozasones. In the cold, unless on long standing, only the carbonyl group reacts with phenylhydrazine, and a hydrazone containing the group

$$-CH(OH)C(N_2H{\cdot}C_6H_5)-$$

is formed; but this compound, on heating with excess of phenylhydrazine, is converted into an osazone, the alcohol group also taking part in the reaction. The molecule of hydrogen which is removed in this process reduces a molecule of phenylhydrazine to aniline and ammonia. Thus with dextrose—

$$CH_2OH[CHOH]_4CHO + 3C_6H_5NH{\cdot}NH_2$$

$$\rightarrow CH_2OH[CHOH]_3C(N_2H{\cdot}C_6H_5)CH(N_2HC_6H_5)$$

Phenylglucosazone.

$$+NH_2C_6H_5 + NH_3 + 2H_2O$$

These osazones have proved of great use in identifying various sugars. Sometimes, however, two distinct sugars yield the same osazone: thus lævulose, like dextrose, gives phenylglucosazone:—

$$CH_2OH[CHOH]_3CO{\cdot}CH_2OH + 3C_6H_5NH{\cdot}NH_2$$

Lævulose.

$$\rightarrow CH_2OH[CHOH]_3C(N_2H{\cdot}C_6H_5)CH(N_2H{\cdot}C_6H_5)$$

Phenylglucosazone.

$$+NH_2C_6H_5) + NH_3 + 2H_2O$$

the α-aldehyde alcohol and the α-keto alcohol yielding the same osazone.

The osazones are crystalline compounds, of a yellow colour, and generally have a definite melting point, by means of which they may be

identified. Concentrated sulphuric acid dissolves the various osazones, giving characteristic colorations, and the solution generally exhibits some particular colour-change on standing (Japp and Klingemann, Ber. 1888, 21, 549). Fuming hydrochloric acid hydrolyses the osazones in the cold into phenylhydrazine and the *a*-dicarbonyl compound from which they are derived (E. Fischer, *ibid.* 1888, 21, 2631).

J. F. T.

HYDRAZOTOLUENE. Prepared by reducing *o*-nitrotoluene in hot alkaline solution with zinc dust or finely divided iron. M.p. 165°.

HYDRAZONE COLOURING MATTERS *v.* Pyrazolone colouring matters.

HYDRINDENE *v.* Ketones and Indene.

HYDRINDONE *v.* Indene.

HYDRIODIC ACID *v.* Iodine.

HYDRIODOL (*cupridol*). A 1 p.c. addition of mercuric iodide to sterilised oil.

HYDROBROMIC ACID *v.* Bromine.

HYDROCARBOSTYRIL *v.* Quinoline.

HYDROCHLORIC ACID *v.* Chlorine.

HYDROCURCUMIN *v.* Turmeric.

HYDROCYANIC ACID *v.* Cyanides.

HYDROERGOTININE (*Ergotoxine*) *v.* Ergot.

HYDROFLUORIC ACID *v.* Fluorine.

HYDROFLUOSILICIC ACID *v.* Fluorine.

HYDROGELS *v.* Colloids.

HYDROGEN. At.wt. 1·0077. Symbol H. The existence of this gas was recognised in the 16th century; its combustible property was discovered in the following century by Turquet de Mayerne, and in 1700 Lemery observed the detonating property of a mixture of air and hydrogen.

Cavendish, in 1766, showed that when the gas was produced from dilute acid and one of the metals, iron, zinc, or tin, it was obtained in amount varying with the metal used.

Hydrogen was for a time confounded with other combustible gases, such as marsh-gas, carbon monoxide, and vapour of ether; all were supposed to contain the same inflammable principle, *phlogiston*, modified by variable amounts of other substances.

Macquer and De la Metherie first observed, in 1766, that water was produced by burning hydrogen, but it was then thought that other products than water were produced at the same time, and Lavoisier made many experiments with the object of detecting the presence of an acid which he imagined should be among the products of combustion, as was the case in the combustion of such bodies as sulphur, carbon, phosphorus, &c. Cavendish, however, in 1781, proved conclusively that water was the only product of combustion when hydrogen burns in air or oxygen, and that if a mixture of hydrogen and oxygen in the proportion of two volumes of the former to one of the latter were burnt, the whole of the gases were converted into water.

Sources. Hydrogen occurs free in nature in the gaseous mixtures evolved from certain volcanos (Bunsen, Ann. Chim. Phys. 1853, [iii.] 38, 215; Deville, Compt. rend. 1862, 55, 75). The gases evolved from Mte. Pelée in Martinique during the eruptions of 1902 contained 22·3 p.c. of hydrogen by volume (Moissan, Compt. rend. 1902, 135, 1085). It also occurs in the jets of steam, known as *fumaroles*, which occur in Tuscany and other places. The gases issuing from the salt beds of Stassfurt (Reichardt, Arch. Pharm. 1860, [ii.] 103, 347; Precht, Ber. 1880, 13, 2326), and Wieliczka (Rose, Pogg. Ann. 48, 353) contain hydrogen, and it also occurs in the gases given off by the oil-wells of Pennsylvania, West Virginia, Ohio, and Indiana (Engler, Ber. 1888, 21, 1816; U.S.A. Geol. Sur. 1909, 2, 297). Hydrogen has been found occluded in certain meteorites (Graham, Proc. Roy. Soc. 1867, 15, 502; Mallet, *ibid.* 1872, 20, 365), and in a large number of minerals (Ramsay and Travers, Proc. Roy. Soc. 1897, 60, 442; Tilden, *ibid.* 1897, 60, 453), and in clays. To a very slight extent, hydrogen occurs free in the atmosphere (Gautier, Ann. Chim. Phys. 1901, [vii.] 22, 5; Liveing and Dewar, *ibid.* 1901, 22, 482; Rayleigh, Phil. Mag. 1902, [vi.] 3, 416; Leduc, Compt. rend. 1902, 135, 860, 1332). According to Claude (Compt. rend. 1909, 148, 1454), there is less than 1 part of hydrogen in one million parts of air. Its presence in the air is probably due to the decomposition of cellulose under the influence of anærobic micro-organisms. Hydrogen is also produced in the decay of various organic bodies, being found in the intestinal gases of many animals (Tappeiner, Ber. 1881, 14, 2375).

Spectroscopic observations have shown that hydrogen completely surrounds the sun, forming an envelope which has received the name of the *chromosphere*. Hydrogen also occurs in certain stars and nebulæ.

In a state of combination, hydrogen forms one-ninth the weight of water and one-fourth the weight of marsh-gas. It also occurs in smaller quantities in combination with phosphorus, sulphur, iodine, bromine, carbon, and nitrogen. It is an essential constituent of all acids; most animal and vegetable substances contain it, and it is a constituent of many minerals. It exists in the air in small quantities in combination with nitrogen as ammonia; and in certain mineral and volcanic springs it is found in combination with sulphur and chlorine as hydrogen sulphide and hydrochloric acid respectively.

Preparation. (1) *Electrolysis of certain aqueous solutions.* Pure hydrogen is readily prepared by the electrolysis of a mixture of 1 part of sulphuric acid and 10 parts of water between platinum electrodes. The potential difference between the terminals must exceed 1·7 volts. The hydrogen is evolved at the cathode, and suitable provision must be made to prevent oxygen from the anode diffusing into the hydrogen. A convenient method consists in immersing the anode in a mass of liquid zinc-amalgam, which absorbs the oxygen completely, forming zinc oxide and eventually zinc sulphate. The current from three or four Bunsen elements is sufficient to work such an electrolytic cell for laboratory use. A suitable piece of apparatus is described in Amer. Chem. J. 1897, 19, 810. A 30 p.c. solution of sodium hydroxide may also be employed; plate nickel electrodes are most convenient, and a useful piece of apparatus for this purpose is described by Vèzes and Labatut (Zeitsch. anorg. Chem. 1902, 32, 464). Hydrogen prepared from sodium hydroxide solution always contains a little organic matter, owing to the presence of carbonate in solution (Morley); it can be obtained quite pure by electrolysing a solution of pure recrystallised baryta (Baker, Chem. Soc. Trans. 1902, 81, 400).

These electrolytic methods are employed on a commercial scale, dilute sulphuric acid being electrolysed between lead electrodes, or sodium or potassium hydroxide between iron electrodes. The chief difficulty encountered is that a mixture of oxygen and hydrogen is given off at both electrodes. The hydrogen contains about 1 p.c. of oxygen, and the oxygen about 2 p.c. of hydrogen. Under certain circumstances this admixture of oxygen may prove dangerous. The introduction of diaphragms increases the resistance of the cell, and is therefore to be avoided if possible. Various patterns of cell have been devised, and are described in J. Soc. Chem. Ind. 1900, 19, 1120; 1901, 20, 258; 1902, 778; 1905, 94; 1905, 1240; 1908, 946; 1909, 799; Eng. Pats. 2820, 1902, and 27249, 1903; Fr. Pats. 355652, 1905, and 397319, 1908; D. R. P. 198626, 1906. The Elektron works at Griesheim use as electrolyte potassium chloride, thereby obtaining potassium hydroxide and chlorine in addition to the hydrogen. The Oerlikon Maschinenfabrik employ the Schmidt process, using potassium carbonate solution, and the Heraeus Company at Hanau a 20 p.c. solution of caustic soda at about 60° (Schuckert process). Large quantities of hydrogen are also made by the Castner-Kellner Company by the electrolysis of common salt solutions. They supply the gas in a compressed state. Other electrolytic processes which have proved commercially successful are those of Garuti Schoop, the International Oxygen Co. of Newark, N.J., Schriver, Churchill, and Burdett. For descriptions of the various cells employed, nature of electrodes, diaphragms, &c., yields, and energy expenditure, *see* Greenwood's Industrial Gases, 1920; C. F. Hale, J. Soc. Chem. Ind. 1921, 40, 122 R.

(2) *Chemical decomposition of water.*—Hydrogen may be prepared by decomposing water; a large number of readily oxidisable substances can be employed for this purpose.

The alkali metals and the metals of the alkaline earths decompose water at ordinary temperatures, liberating hydrogen and producing the corresponding metallic hydroxide. The action is very violent, particularly with potassium, rubidium, and caesium. The reactions can be readily controlled, however, by employing the amalgams of these metals. The action of steam on pure sodium has been used for the preparation of pure hydrogen (Scott, Phil. Trans. 1893, 184, 548; Mellor and Russell, Chem. Soc. Trans. 1902, 81, 1279), and the use of sodium, mixed with oil, aluminium, and infusorial earth, for the preparation of hydrogen on a commercial scale has been patented (U.S. Pats. 883531, 1908; 909536, 1909).

Magnesium decomposes water at temperatures above 70° (Ditte, Compt. rend. 1871, 73, 108), and burns vigorously when heated in steam. Magnesium amalgam decomposes cold water (Fleck and Basset, J. Amer. Chem. Soc. 1895, 17, 789).

Aluminium does not decompose water unless some means is afforded of removing the oxide from the surface of the metal. This is easily effected by amalgamating it with $\frac{1}{8}$ its weight of mercury, when the amalgam produced readily decomposes water and can be employed as a source of pure hydrogen (Baille and Féry, Ann. Chim. Phys. 1889, [vi.] 17, 246; Wislicenus and Kauffmann, Ber. 1895, 28, 1323). Hydrogen is readily obtained pure by slowly adding water to a mixture of fine aluminium filings containing 1 to 2 p.c. of mercuric chloride and 0·5 p.c. of potassium cyanide, keeping the temperature at 70° (Mauricheau-Beaupré, Compt. rend. 1908, 147, 310; Fr. Pat. 392725, 1908). One kilo. of this mixture yields 1300 litres of hydrogen.

At a red heat, water vapour is easily decomposed by iron, hydrogen and triferric tetroxide being produced (Lavoisier, Œuvres, 2, 360). This method is employed on a large scale and has been the subject of numerous patents (Eng. Pats. 7518, 1887; 20752, 1890; 4134, 1891; 28721, 1896; 10356, 1903; 21479, 1908; 17591, 1909; 12117, 1912; Fr. Pats. 373271, 1907; 386991, 1908; 395132, 1908; 444105, 1912; 461480, 461623, 461624, 1913; U.S. Pat. 971206, 1908; D. R. PP. 226453, 1909; 254222, 263390, 263391, 268062, 268339, 1912; *cf.* Bergius, J. Soc. Chem. Ind. 1913, 32, 462. The oxide produced is reduced to metal by heating with coal or by treatment with water gas as in the Messerschmidt process, or by either carbon or carbon monoxide as in the Bergius process, and used again.

Steam is readily decomposed by passing it over red-hot coke, when a mixture consisting essentially of carbon monoxide and hydrogen in approximately equal volumes, is produced, known as *water-gas* (*v.* Gas, water). Numerous methods have been proposed for the purpose of preparing hydrogen commercially from this mixture. In one process (Frank, Fr. Pat. 371814, 1906), the dried mixture is passed over calcium carbide at a temperature above 300°, when carbon monoxide and dioxide react with the carbide, forming calcium oxide, carbonate and carbon, while the nitrogen present is converted into calcium cyanamide. The oxides of carbon may be partially removed by a preliminary cooling process, whereby the monoxide is liquefied and the dioxide solidified. Jouve and Gautier (Fr. Pat. 372045, 1906) propose to pass the gas through a porous partition in order to separate the hydrogen by reason of its rapid power of diffusion. It is said that by one such operation the percentage of carbon monoxide may be reduced from 45 to 8 p.c. In other processes, the carbon monoxide is removed by chemical means; for this purpose it is passed over a catalyser, *e.g.* ferric oxide, heated to 400°–500° with excess of steam, when the monoxide is replaced by an equal volume of hydrogen, carbon dioxide being produced, which may be removed by solution in water or by absorbing it in milk of lime (Henry and Hembert, Compt. rend. 1885, 101, 797; D. R. P. 224862, 1907; Claude, *idem.* 1921, 173, 653).

The oxidation of carbon monoxide by steam with the liberation of hydrogen can be effected at 400°–500° in the presence of reduced iron or nickel (Fr. Pats. 355324, 1905; 375164, 1906; *cf.* Mond and Langer, Eng. Pat. 12608, 1888, and Fr. Pat. 361429, 1905).

The Griesheim Elektron Company (Eng. Pat. 13049, 1912, J. Soc. Chem. Ind. 1913, 278) pass water-gas mixed with steam, into a heated retort containing lime, when the oxides of carbon are removed as calcium carbonate. In the Linde-Frank-Caro process water-gas is first treated with lime or a solution of caustic soda to remove carbon dioxide, and is then subjected to pressure and cooled with liquid air whereby carbon monoxide, nitrogen, and other impurities are liquefied whilst the hydrogen still remains gaseous. The liquid carbon monoxide can be burnt in a gas engine and so serve to drive the plant. By further treatment hydrogen of 99·2-99·4 p.c. purity is obtained which may be employed for filling balloons or for catalytic reactions. (For a method of determining small quantities of carbon monoxide in hydrogen, *see* S. K. Rideal and Taylor, Analyst, 1919, 89.)

Hydrogen free from compounds of carbon and oxygen, can be prepared by heating coke, impregnated with 10 p.c. potassium carbonate and mixed with five times its weight of burnt lime, in a current of steam at 550°-750° (Eng. Pat. 8734, 1910).

The decomposition of steam may also be effected by passing it over red-hot barium sulphide, which becomes oxidised to sulphate, with the simultaneous formation of hydrogen (Fr. Pat. 361866, 1905). The sulphate is reduced with coal or producer gas to sulphide, and used again.

(3) *Action of metals on acids.*—The commonest method of preparing hydrogen for laboratory purposes consists in acting upon granulated zinc with either dilute hydrochloric acid (1 of acid to 2 of water), or sulphuric acid (1 of acid to 8 of water), when hydrogen is evolved and zinc chloride or sulphate is left in solution. Very pure hydrogen is obtained from pure zinc and pure diluted acid, but the action is extremely slow. A regular stream of the gas may be obtained, however, by adding a little platinic chloride solution. Platinum is deposited over the surface of the zinc, and the liberated hydrogen escapes freely from the surface of the platinum, leaving the zinc surface free from bubbles of gas (Gourdon, Compt. rend. 1873, 76, 1250). A similar effect is produced by adding a small quantity of a salt of copper, silver, gold, tin, antimony, bismuth, nickel, or cobalt.

The apparatus shown in the annexed figure may be used for obtaining pure hydrogen for laboratory purposes (Edwards, J. Ind. Eng. Chem. 1919, 11, 961). The apparatus is exhausted through *a*, whilst the tube *d*, which dips into mercury, serves as an indicator of the residual pressure and as a safety valve. The acid flask, *f*, is nearly filled with dilute sulphuric acid (1 : 8) and contains a few fragments of zinc, so that the hydrogen evolved will sweep out all air. The vent *e* is then closed until the pressure of the gas is sufficient to force the acid into the tube, to free the connections from air. The tube beyond the tap, *b*, enters the generator through a rubber stopper, which is always under liquid. The rate of generation of the gas is controlled by the tap *c* (J. Soc. Chem. Ind. 1920, 20 A).

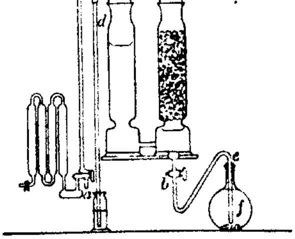


FIG. 1.

Other metals, *e.g.* aluminium, magnesium, and iron, may be used instead of zinc for generating hydrogen from acids. Pure hydrogen is readily prepared by acting upon aluminium with mercuric chloride solution slightly acidified with hydrochloric acid (Bodenstein, Zeitsch. physikal. Chem. 1897, 22, 3). The use of zinc, and more particularly of iron and sulphuric acid upon a commercial scale, is very common (*v.* Eng. Pats. 15509, 1897; 10277, 1896; 17515, 1898; 25084, 1897).

(4) *Action of metals and non-metals on alkalis.* The metals zinc, aluminium, and tin readily dissolve in warm concentrated alkali hydroxide solutions, liberating hydrogen and forming alkali zincate, aluminate, and stannate respectively. Very pure hydrogen is thus produced from aluminium free from carbon. The non-metallic element, silicon, similarly dissolves, and considerable quantities of hydrogen may be prepared by heating powdered silicon or ferrosilicon with sodium hydroxide solution and milk of lime (D. R. P. 216768, 1908; Eng. Pat. 21032, 1909) (*v. infra, Hydrogen for Balloons*).

Hydrogen may be prepared by heating slaked lime with either zinc dust (Schwarz, Ber. 1886, 19, 1141) or coal. The resulting calcium carbonate in the latter process may be reconverted into slaked lime by heating in steam (Bloxam).

(5) *Decomposition of metallic hydrides.*—The hydrides of the alkali metals and those of the alkaline earths readily decompose water at ordinary temperatures, liberating hydrogen and forming the corresponding metallic hydroxide. The use of calcium hydride for preparing hydrogen is very convenient, since the hydride is readily portable, and each gram of the substance yields more than 1 litre of hydrogen when decomposed by water. The hydrogen liberated is twice that which is absorbed by the metallic calcium in the preparation of the hydride (Fr. Pat. 327878, 1902); (*v. infra, Hydrogen for Balloons*).

Palladium, especially when amorphous, capable of adsorbing large quantities of hydrogen; from the substance thus produced, pure hydrogen is readily obtained by heating it under reduced pressure (*v. infra*).

Purification.—The electrolysis of either dilute sulphuric acid or a solution of pure baryta, yields practically pure hydrogen, as also does the action of steam on pure sodium. Most methods of preparation, however, yield hydrogen containing more or less of a number of impurities, nearly all of which may be removed by treating the gas with reagents capable of absorbing them. The precise nature of most of the impurities depends upon the method of preparation employed, but one in particular, viz. atmospheric air, is common to nearly all methods. Its presence in the gas is due partly to its presence in the liquids employed in the preparation of the gas, a source of error which may be diminished by previously boiling the solution, partly to the difficulty of completely expelling air from the apparatus, and partly owing to leakage into the apparatus through cork or rubber joints, which should therefore be as few as possible. The oxygen thus introduced may be removed by passing the gas over red-hot copper or spongy platinum or through chromous chloride solution, but the nitrogen cannot be similarly removed.

A convenient but expensive method of obtaining pure hydrogen consists in passing the dried, approximately pure gas over palladium, the metal having been previously strongly heated, introduced into a tube fitted with a stopcock and the tube evacuated. The metal is allowed to cool during the absorption of the gas. The gas left in the apparatus is finally pumped out From the palladium hydrogen, pure hydrogen is readily obtained by attaching the palladium tube to the apparatus into which the gas is to be introduced, and gently warming the metal

Hydrogen prepared from acid and ordinary iron, which contains a certain amount of carbide, invariably contains gaseous hydrocarbons which give the gas an unpleasant odour, and this method of preparation is never used for laboratory purposes. The hydrocarbons may be removed by passing the gas through alcohol, or a tube filled with pieces of wood-charcoal or paraffin (Stenhouse, Annalen, 1858, 106, 125; Varenne and Hébré, Bull. Soc. chim. 1877, [ii.] 28, 523).

According to Morley, the purest redistilled zinc always contains a little occluded oxides of carbon, which find their way into hydrogen prepared from the metal and acid. The commercial metal may also contain, besides a little lead, traces of sulphur, arsenic, antimony, carbon, silicon, and even phosphorus, which cause the hydrogen generated from the metal by means of acid to contain the corresponding gaseous hydrides. Sulphuric acid may contain sulphur dioxide, which will be partly evolved with the hydrogen and partly reduced to hydrogen sulphide (Kolbe, Annalen, 1861, 119, 174), and also nitrogen compounds, which lead to the formation of nitrogen and nitrous oxide in the hydrogen. Frequently sulphuric acid contains arsenic and selenium, which leads to the formation of the corresponding hydrides. Hydrochloric acid prepared from sulphuric acid may contain the same impurities.

Sulphur dioxide, the hydrides of sulphur, selenium, silicon, and hydrogen chloride carried over by the hydrogen may be absorbed in a solution of potassium hydroxide. The hydrides of phosphorus, arsenic, and antimony may be absorbed by solutions of various metallic salts, *e.g.* mercuric chloride, lead nitrate, or silver sulphate (Dumas, Ann. Chim. Phys. 1843, [iii.] 8, 189).

All the above impurities are decomposed when the hydrogen is passed over red-hot copper turnings. The small quantity of nitrogen that may be introduced by the decomposition of oxides of nitrogen is usually not inconvenient.

For laboratory purposes, hydrogen is best purified from phosphine, arsine, and stibine, by passing it through saturated permanganate solution and then through 5–10 p.c. silver nitrate. After washing hydrogen with concentrated permanganate solution, however, the gas contains traces of oxygen For removing traces of arsine from large quantities of hydrogen, bromine is the best absorbent; on a technical scale potassium hypochlorite or bleaching powder may be substituted (Reckleben and Lockemann, Zeitsch angew. Chem. 1908, 21, 433).

Arsine is said to be completely removed from hydrogen by bubbling the gas through petroleum spirit cooled by liquid air to −110°, and the process has been recommended for technical use (Compt. rend. 1903, 136, 1317).

An elaborate method for purifying hydrogen by freezing out the impurities is described by Kamerlingh Onnes (Proc. K. Akad. Wetensch. Amsterdam, 1909, 11, 883): using 25 litres of liquid air, 10,000 litres of hydrogen can be purified in 8 hours.

Hydrogen may be dried for ordinary purposes by passing it over anhydrous calcium chloride or through concentrated sulphuric acid. The latter process, however, slightly contaminates the gas with sulphur dioxide (Dittmar and Henderson, Proc Roy. Soc. Glasgow, 1891, 22, 33; Berthelot, Compt. rend. 1897, 125, 743; Milbauer, Zeitsch physikal. Chem. 1907, 57, 649). The use of phosphoric anhydride, free from lower oxides, is to be preferred

Properties.—Hydrogen is a colourless, odourless, tasteless gas. It is the lightest gas known, 1 litre of hydrogen at N.T.P. and at sea-level in lat 45°, weighs 0·089873±0·000027 gram (Morley, Zeitsch physikal. Chem. 1896, 20, 242; *cf.* Regnault, Relation des Expér 2, 121; Leduc, Compt. rend. 1891, 113, 186; Thomsen, Zeitsch. anorg. Chem. 1896, 12, 1). The density of hydrogen compared with air is therefore 0·0694. The product *pv*, instead of being constant as Boyle's law demands, continually increases as the pressure is increased. At 200 atmos. (absolute) it is 1·134 (Amagat, Ann. de chim. et de Phys. [6] 29, 1883, 68). The coefficient of thermal expansion at constant pressure is 0·003661 (Regnault), and at constant volume the coefficient is 0·0036624 (Chappuis). The thermal conductivity of hydrogen is seven times that of air (Stefan). Between 0° and 200° the molecular specific heat at constant pressure is 6·81 and at constant volume is 4·81 calories. The specific heat increases with rise of temperature. According to Mallard and Le Chatelier (Compt. rend. 1887, 104, 1780), the mean molecular specific heat of hydrogen at constant pressure between 0° and t° is $6{\cdot}5+0{\cdot}0006\,(t+273)$; the value at constant volume is $4{\cdot}700+0{\cdot}00045t$ (Pier, Zeitsch. Elektrochem. 1909, 15, 536). According to Crofts, $C_p=4{\cdot}86+0{\cdot}00064t$, where C is the mean specific heat between t and 15° (Chem. Soc. Trans. 1915, 290). The ratio of the specific heats is 1·405 (Röntgen). Hydrogen is diamagnetic.

Hydrogen is very slightly soluble in water, its absorption-coefficient between 0° and 25° being given by the formula

$$0{\cdot}021528-0{\cdot}00019216t+0{\cdot}000001728t^2$$

(Timofejeff, Zeitsch. physikal. Chem. 1890, 6, 141; *cf.* Winkler, Ber. 1891, 24, 89; Bohr and Bock, Wied. Ann. 1891, 44, 316; Geffken, Zeitsch. physikal. Chem. 1904, 49, 257). For its solubility in alcohol, *v.* Timofejeff, *l.c.*, and in various aqueous salt solutions, *v.* Geffken, *l.c.*

The liquefaction of hydrogen for many years presented the most difficult problem to experimenters on the liquefaction of gases. In 1877, Cailletet submitted hydrogen to the same process as he had successfully used in the liquefaction of oxygen and nitrogen, and observed the formation of a fine mist when hydrogen was subjected to a pressure of 280 atmos. and then suddenly released. In 1884 Wroblewski (Compt. rend. 1884, 100, 979) liquefied hydrogen by cooling the gas, under a pressure of 190 atmos., by means of boiling nitrogen, and then quickly releasing the pressure. By a similar method, Olszewski (Compt. rend 1884, 99, 133; 1885, 101, 238) succeeded in obtaining colourless drops of liquid hydrogen Dewar (Chem. Soc. Proc. 1895, 229; Chem. Soc. Trans. 1898, 528; Proc Roy. Soc. 1901, 68, 260) was the first to succeed in preparing liquid hydrogen in sufficient quantity to show a definite meniscus by applying the regenerative process to the compressed gas after first cooling it to −205°. Travers (Phil. Mag. 1901, [vi.] 1, 411), Olszewski (Ann Chim Phys. 1903, [vii.] 29, 289), and Nernst and Pollitzer (Zeitsch. Elektrochem. 1911, 17, 735) have described processes whereby liquid hydrogen may be prepared in quantity.

Liquid hydrogen forms a clear, colourless liquid, boiling at −252·5° (Dewar, Proc Roy. Soc. 1898, 63, 256; Travers, Phil. Mag. 1902, [vi.] 3, 535). The vapour pressures of the liquid at various temperatures between 24·59° and 32·93° (abs.) have been measured by Cath and Kamerlingh Onnes, and may be represented by the formula $T \log p = -56{\cdot}605 + 3{\cdot}8015T - 0{\cdot}10458T^2 + 0{\cdot}003321T^3 - 0{\cdot}000005102T^4$, in which p=pressure in international atmospheres Liquid hydrogen has the greatest specific heat of any liquid, namely 6·4 (Dewar) (*cf.* Keesom and Onnes K. akad. Amsterdam Proc. 20, 1000, 1918). When cooled by rapid evaporation under diminished pressure, the liquid solidifies to a transparent solid, melting at −257° (Dewar) or −258·9° (Travers, Proc. Roy. Soc. 1902, 70, 484), and having a sp.gr. at −259·9° of 0·0763 (*ibid.* 1904, 73, 251). According to Kamerlingh Onnes and Crommelin the density of liquid hydrogen increases from 0·07086 at the boiling-point (−252·77°) to 0·07631 at −258·27°. Contraction occurs on freezing, and at −262·0° the density of solid hydrogen is 0·08077. The density of liquid hydrogen at the triple point (−159·2°) is 0·07709, and on the assumption that the density of solid hydrogen at this temperature does not differ appreciably from that at −162°, the contraction on freezing is about 4·8 p.c. of the liquid volume. Augustin (Ann. Physik. 1915, [iv.] 46, 419) found the density of liquid hydrogen 0·07105 at −252·83° and 745·42 mm. The refractive indices obtained by the method of total reflexion were at this temperature and pressure λ656·3, 1·10924; λ579·0, 1·10974; λ546·1, 1·11003; λ465·9, 1·11179; λ404·7, 1·11262 (Augustin, *l.c.*). According to Verschaffelt the viscosity of liquid hydrogen at 20·43° (abs.) is 0·00013. For the vapour of hydrogen it is 0·000010. The critical pressure of hydrogen is 15 atmos. and its critical temperature is −243° to −241° (Dewar) (33·18° (abs.) and 12·8 atmos. (Onnes, Crommelin, and Cath).

Apparatus for liquefying hydrogen. The apparatus works on Linde's principle, with preliminary cooling by means of liquid air. It is so arranged that many experiments can be carried out in the apparatus itself, without transferring the liquefied hydrogen; to this end the liquefying chamber is closed air-tight, and a special small vacuum vessel provided for the collection of the liquid. The compressed hydrogen enters by the middle tube, shown thickened in the sections of the spirals, then enters the bath of liquid air, through which it passes in a great number of windings (*b*) of very fine spiral copper tube, thence into the sheet brass vessel (*c*) in 26 windings, where it expands, cools, and liquefies. After passing at V a valve (not shown in the figure) and expanding nearly to atmospheric pressure, it leaves, through a similar number of windings, to utilise its low temperature as far as possible, by the tube shown. The evaporated air also leaves by a third spiral tube (*d*), to utilise its cold. The axial tube with cross pieces (one to a manometer, the other fitted with a cork which will yield in case of rise of pressure through any stoppages) is of German silver, and is 2½ cm. wide. It permits of the entry of, for example, the little apparatus shown, for specific heat determinations. The brass vessel can be separated into two halves, to allow the little vacuum vessel shown to be placed in position. With a passage of 2–3 cb. m. of hydrogen gas per hour the hourly yield of liquid is 300–400 c.c., or about 10 p.c., and the consumption of liquid air about 0·3 litre. The apparatus, when used, is first warmed, and the hydrogen from a compressor or cylinder passed through till all is quite dry. Then liquid air is passed in from the vacuum vessel on the left till the brass vessel is covered, and the apparatus left to itself till the whole has reached the temperature of liquid air. Hydrogen at 150 atmospheres is now passed in, and after about ten minutes liquifaction begins. If needed,

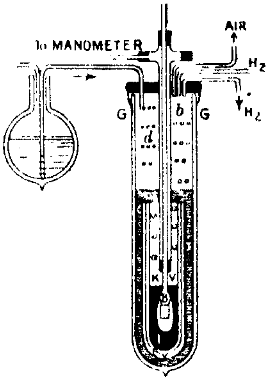


Fig. 2.

the hydrogen can be transferred by a siphon vacuum-tube with a gauze filter on the end to stop any accidental frozen air. Very pure hydrogen must be used; with a cylinder it is possible to work till the pressure is reduced from 150 to 70 atmospheres—with a compressor, practically all the hydrogen can of course be utilised, whilst with a cylinder nine-tenths of it is lost (Nernst, Zeitsch. Elektrochem. 1911, 17, 735; J. Soc. Chem. Ind. 1911, 30, 1159).

The spectrum of hydrogen consists essentially of four bright lines—one in the red, corresponding with Fraunhofer's dark line C, and one in the greenish-blue, coincident with the dark line F. Their wave-lengths are (Angström) C=6562, F=4861, blue=4340, indigo=4101 in ten-millionths of a millimetre.

Hydrogen is an inflammable gas, burning in air or oxygen with an extremely hot, almost colourless flame, and producing water. Even with pure hydrogen, however, the centre of the flame is coloured green, while the external portions are of a violet-blue colour. On reducing the pressure, the blue colour is transformed to green, and from that successively to yellow, orange, and red. Under increased pressure, hydrogen burns with a luminous flame.

The combination of hydrogen and oxygen proceeds slowly at ordinary temperatures in the presence of sunlight (Baker, Chem. Soc. Trans. 1902, 81, 400). The rate of combination is slow at 180° (Gautier and Hélier, Bull. Soc. chim. 1896, [iii.] 15, 468), but with rise of temperature it becomes quicker and quicker, and explosion occurs at about 550° (Gautier and Hélier, *l.c.*; Berthelot, Compt. rend. 1897, 125, 271; Ann. Chim. Phys. 1898, [vii.] 13, 30; Meyer and Raum, Ber. 1895, 28, 204; Bone and Wheeler, Phil. Trans. 1906, A, 206, 1; Rowe, Zeitsch. physikal. Chem. 1907, 59, 41). Mixtures of the two gases, if perfectly pure and dry, may be heated to the melting-point of silver without combination occurring (Baker, *l.c.*). The ignition-points of various mixtures of oxygen and hydrogen, from $3H_2+O_2$ to H_2+4O_2, vary between 557° and 507° when fired by adiabatic compression, electroyltic gas having an ignition-point of 536° (Dixon, Chem. Soc. Trans. 1910, 97, 661; *cf.* Falk, J. Amer. Chem. Soc. 1906, 28, 1517; 1907, 29, 1536). The union of hydrogen and oxygen proceeds quickly at ordinary temperatures in the presence of finely divided palladium, platinum, iridium, osmium, or gold.

Mixtures of air and hydrogen are explosive within the limits 74·2–4·1 p.c. of hydrogen (Coward, Chem. Soc. Trans. 1914, 1859; Coward, Carpenter, and Payman, *idem.* 1919, 27).

Hydrogen unites at 250° with sulphur and selenium, and at 400° with tellurium. It can be made to unite directly with nitrogen under the influence of the silent discharge (Chabrier, Compt. rend. 1872, 75, 489; Donkin, Proc. Roy. Soc. 1881, 31, 281) or of electric sparks (Berthelot, Ann. Chim. Phys. 1880, [v.] 21, 285); for its combination with nitrogen under the influence of high pressure, temperature, and catalysts, *see* AMMONIA, SYNTHESIS OF. Compounds of hydrogen with arsenic, phosphorus, antimony, boron, and silicon, can be prepared indirectly.

Hydrogen unites with pure carbon directly when heated to 1150°, methane being produced (Bone and Jerdan, Chem. Soc. Trans. 3897, 71, 41; Bone and Coward, 1908, 93, 1975; 1910, 97, 1219). By passing an electric arc between carbon poles in an atmosphere of hydrogen, acetylene is produced, accompanied by a little methane and ethane (Berthelot, Compt. rend. 1862, 54, 640; Bone and Jerdan, Chem. Soc. Trans. 1901, 79, 1062).

Gaseous hydrogen combines with fluorine even in the dark and at ordinary temperatures, with explosive violence, hydrogen fluoride being produced (Moissan, Ann. Chim. Phys. 1891, [vi.] 24, 224). With liquid fluorine at −210°, explosion also occurs, and a similar result follows on mixing solid fluorine and liquid hydrogen (Moissan and Dewar, Bull. Soc. chim. 1897, [iii.] 17, 932; Compt. rend. 1903, 136, 641).

Chlorine does not combine appreciably with hydrogen at ordinary temperatures in the dark, but only when heated above 400° or exposed to light. In diffused light, combination occurs slowly, and there is usually an initial *period of induction* (Bunsen and Roscoe, Phil. Trans. 1857, ii. 378) during which the rate of combination slowly increases to its maximum value and afterwards remains constant. This period of induction is due to the presence of traces of volatile impurities (Burgess and Chapman, Chem. Soc. Trans. 1906, 89, 1399). Under the direct action of actinic rays, mixtures of hydrogen and chlorine explode.

Hydrogen combines directly with bromine above 400°, and slowly even at 100° in the presence of light (Kastle and Beatty, Amer. Chem. J. 1898, 20, 159). With iodine, the rate of combination becomes measurable above 200°.

The alkali metals, when heated to 360° in hydrogen, directly absorb the gas, forming white solid hydrides of the type MH (Guntz, Compt. rend. 1896, 122, 244; Moissan, Bull. Soc. chim. 1902, 27, 1141; Ann. Chim. Phys. 1905, [viii.] 6, 289, 323; Holt, Chem. Soc. Abstr. 1909, ii. 807). The alkaline-earth metals similarly combine with hydrogen, yielding solid hydrides of the type RH_2 (Moissan, Bull. Soc. chim. 1899, [iii.] 21, 876; Guntz, Compt. rend. 1901, 133, 1209). According to Winkler (Ber. 1891, 24, 884), hydrogen combines directly with various finely divided metals, *e.g.* cerium, yttrium, lanthanum, obtained by reducing their oxides with magnesium powder.

Hydrogen is a reducing agent, and readily displaces a large number of metals from their compounds with oxygen, sulphur, chlorine, &c. Thus the oxides of copper, lead, iron, antimony, &c., are easily reduced to the metallic state, with the formation of water, when heated in a current of hydrogen to a more or less elevated temperature. Silver oxide is slowly reduced at ordinary temperatures, and rapidly and completely at 100° (Colson, Compt. rend. 1900, 130, 330), a reaction which may be used to determine hydrogen in gaseous mixtures. Palladous oxide is reduced in the cold by hydrogen (Wöhler, Annalen, 1874, 174, 60), as also is the corresponding chloride, either in the anhydrous state or in solution (Phillips, Amer. Chem. J. 1894, 16, 255; Campbell and Hart, *ibid.* 1896, 18, 294).

When hydrogen is passed through a solution of silver nitrate, sulphate, or acetate, metallic silver is precipitated; the amount of metal thus separated is small compared with that left in solution. The reaction is carried further by raising the temperature, and the precipitated metal is very pure. Palladium, platinum, and gold are similarly precipitated. Under great pressures, such reductions are much more complete. Thus silver and mercury are quantitatively precipitated from solutions of their salts at ordinary temperatures under 200 atmos. pressure. At higher temperatures, nickel, cobalt, lead, and bismuth are similarly precipitated, the deposition of nickel being complete at 200° and 180 atmos. (Ipatieff and Werchowsky, Ber. 1909, 42, 2078).

Occluded hydrogen (v. *infra*) is capable of bringing about a great number of chemical changes that the free gas is unable to effect. Thus hydrogen occluded in palladium will unite with chlorine, iodine, and oxygen, even in the dark, at ordinary temperatures (Böttger, Ber. 1873, 6, 1396). It also reduces chlorates to chlorides; nitrates to nitrites and even to ammonia; mercuric chloride to mercurous chloride; ferric salts to ferrous salts; ferricyanides to ferrocyanides; and indigo-blue to indigo-white (Gladstone and Tribe, Chem. News, 1878, 37, 68). A number of these reactions can be utilised in quantitative analysis (Chapman, Analyst, 1904, 29, 346). Hydrogen occluded in platinum or copper produces similar changes.

Hydrogen also becomes much more chemically active in contact with various finely divided metals, such as platinum black and nickel, cobalt, iron and copper reduced from their oxides. Thus, hydrogen and oxygen combine rapidly, at ordinary temperatures, in the presence of platinum black. The union of the gases is started by the heat evolved as they are occluded, and, once started, combination proceeds quickly, the metal being heated so much that it becomes incandescent. Similarly, at 400° hydrogen and iodine vapour rapidly unite in the presence of platinum black.

A very general method of reduction and hydrogenation has been based upon the fact that hydrogen becomes chemically active in the presence of finely divided nickel that has been just previously reduced from its oxide. The best product is formed by calcining nickel nitrate at a low red heat and reducing the oxide at about 300°. The temperature of reduction greatly affects the activity of the nickel. It is further affected by the presence of certain substances, like sulphur, phosphorus, and arsenic, which inhibit the catalytic action of the metal. By passing the vapours of a large number of substances, mixed with hydrogen, over reduced nickel at quite moderate temperatures, reductions are easily effected; thus nitrous oxide produces nitrogen and water, nitric oxide and nitrogen peroxide are reduced to ammonia, and the oxides of carbon are converted into methane. Many substances in the state of liquids may be hydrogenated or reduced under particular pressures and temperatures, and the course of the reaction is occasionally modified by the material of the vessel in which it is effected. Organic nitro compounds, fatty or aromatic, are reduced to amines. Unsaturated fatty hydrocarbons are transformed into paraffins, while benzene and numerous derivatives are easily converted into hexahydrobenzene and its substitution-products. Aldehydes and ketones are reduced to alcohols with remarkable ease. Indigo blue is reduced to indigo white, and leuco derivatives of other vat dyes may be similarly obtained. The nickel is not altered, and permits of hydrogenation being carried on indefinitely. In certain cases other metals, *e.g.* cobalt, iron, copper, platinum may be used, but nickel is found to be the most generally applicable. The hydrogen must be carefully freed from impurities which under its action and the catalyst after a time loses its activity, which, however, can be renewed by appropriate treatment. (Sabatier and Senderens, Compt. rend. 1897, 124, 1358; 1899, 128, 1173; 1900, 130, 1559, 1628, 1761; 131, 140; 1901, 132, 210, 566, 1254; 133, 321; 1902, 134, 514, 689, 1127; 135, 87, 225; 1903, 136, 738, 921, 983; 137, 301, 1025; 1904, 138, 457, 1257; 1905, 140, 482; Bull. Soc. chim. 1905, [iii.] 33, 263; Ann. Chim. Phys. 1905, [viii.] 4, 319, 433; Sabatier and Mailhe, Compt. rend. 1903, 137, 240; 1904, 138, 407, 245; 1905, 140, 350; 1906, 142, 553; 1907, 144, 824, 955, 784, 1086; 145, 18, 1126; 1908, 146, 457, 1193; Ann. Chim. Phys. 1909, [viii.] 16, 70); Ipatiev and others, various papers in J. Russ. Phys. Chem. Soc. 1906 *et seq.* *Cf.* Sabatier, La Catalyse en Chimie Organique; *see* art. Catalysis; also Henderson's Catalysis in Industrial Chemistry, Longman's Series of Monographs on Industrial Chemistry.) Many processes of hydrogenation under the influence of catalysts are reversible; by modifying the conditions, particularly of temperature, dehydrogenation may take place; thus, cyclic compounds may be regenerated from their hydrogenated derivatives, hydrocarbons may be degraded, and aldehydes and ketones may be formed from their respective primary and secondary alcohols.

Certain chemical systems which lead to the liberation of hydrogen are capable of acting as reducing agents when another substance is added to them that is capable of being reduced. Thus a solution of potassium chlorate remains unaffected when hydrogen is passed through it, but reduction to chloride readily occurs if zinc and sulphuric acid are added to the solution. Other systems are furnished by the alkali metals or their amalgams in contact with water, which are capable, among other things, of reducing aldehydes and ketones to alcohols; and zinc, iron, or tin, with either hydrochloric, sulphuric, or acetic acid, systems which are capable of reducing nitro compounds to amines, &c. Hydrogen evolved from such systems therefore appears to possess an activity superior to that of the ordinary gas; it is termed *nascent* hydrogen.

The superior activity possessed by hydrogen at the moment of its liberation is supposed by some chemists to be due to the fact that the gas is liberated in the atomic state, and is therefore more capable of entering into chemical reactions than after it has assumed the molecular state, since the combination of atoms to form molecules is accompanied by the degrading of a certain amount of energy. That this cannot be a full explanation is seen, however, by the fact that a reduction effected by one system evolving nascent hydrogen is not necessarily effected by another system, *e.g.* the system zinc and dilute sulphuric acid will reduce chlorates to chlorides, but the system sodium-amalgam and water will not. For evidence for the dissociation of hydrogen into atoms at high temperatures, *see* Langmuir and Mackay (J. Amer. Chem. Soc. 1914, 36, 1708; Langmuir, *ibid.* 1912, 34, 1310; Freeman, *ibid.* 1913, 35, 927).

Adsorption of hydrogen by metals. In 1863, Deville and Troost (Compt. rend. 1863, 57, 894) observed that red-hot platinum and iron were permeable to hydrogen. Upon further investigating this subject, Graham (Proc. Roy. Soc. 1867, 15, 223; 1868, 16, 422; 1869, 17, 212, 500) found that palladium possessed this property in a much higher degree, and, further, he showed that there was no need to assume a porosity in the structure of these metals to account for this phenomenon, but that it was due to the fact that such metals absorb hydrogen, yielding substances which still retain metallic lustre and characteristic metallic properties, but which readily evolve the absorbed gas under altered conditions. To this property, Graham gave the name *occlusion.* It may be studied by placing the metal within a porcelain tube, glazed inside and out, evacuating it by means of a mercury pump and heating to redness. Hydrogen is then admitted and allowed to flow over the metal while it cools. The tube is then evacuated again and the contents heated to redness once more, by which means the occluded hydrogen is expelled from the metal, and may be pumped off and measured.

The amount of hydrogen adsorbed depends to some extent on the physical condition of the metal. In one experiment, a palladium wire was found by Graham to absorb 935 times its own volume of hydrogen. Mond, Ramsay, and Shields (Phil. Trans. 1895, A, 186, 657; 1897, A, 190, 129; 1898, A, 191, 105) have shown that palladium black adsorbs at the ordinary temperature 873 to 889 volumes of hydrogen, and that palladium wire and sponge adsorb a similar amount. Amorphous palladium is more active than the crystalline variety, especially at low temperatures (*cf.* Holt, Edgar, and Firth, Zeitsch. physikal. Chem. 1913, 82, 513; Andrew and Holt, Proc. Roy. Soc. 1913, [A] 89, 170; Holt, *idem*, 1914, [A] 90, 226; Firth, Chem. Soc. Trans. 1920, 171). Palladium-hydrogen readily evolves hydrogen in a vacuum, that prepared from the 'black' at the ordinary temperature, while the substance obtained from the foil requires warming to 100°. In all cases, however, a red heat is required to drive off the last traces of gas. Even at a red heat, however, palladium still adsorbs large quantities of hydrogen if the pressure is sufficiently increased (Dewar, Chem. Soc. Proc. 1897, 192; Berry, Chem. Soc. Trans. 1911, 99, 463; Sieverts, Zeitsch. physikal. Chem. 1914, 88, 103, 451). Hydrogen which has been ionised by the action of Röntgen rays or by β and γ rays from radium will not diffuse through a palladium plate at the ordinary temperature (Sieverts). According to Sieverts, Jurisch, and Metz (Zeitsch. anorg. Chem. 1915, 92, 329) the solubility is proportional to the square root of the pressure and diminishes with increasing temperature. Although hydrogen is insoluble in pure silver, the addition of silver to palladium greatly increases the solubility, until a maximum is reached at all temperatures at 40 p.c. Ag, beyond which it again falls rapidly. At 138° an alloy containing 40 p.c. Ag dissolves more than four times as much hydrogen as pure palladium, the solubility becoming *nil* at 70 p.c. Ag. Platinum added to palladium diminishes the solubility. Small quantities of hydrogen sulphide adsorbed by palladium entirely prevent the occlusion of hydrogen by that metal (*cf.* Maxted, Chem. Trans. 1919, 115, 1050).

Palladium readily adsorbs 935 vols. of hydrogen if it is employed as negative electrode in a water voltameter. Should the electrolysis be continued beyond this point, the metal becomes supersaturated with gas; the excess is, however, evolved as soon as the current ceases (Thoma, Zeitsch. physikal. Chem. 1889, 3, 69).

Colloidal palladium and platinum solutions adsorb hydrogen very readily and in large amounts (Kernot and Niguesa, Rend. accad. Sci. Fis. Mat. Napoli, 1909, [iii.] 15, 168). Various other metals, *e.g.* iron, nickel, cobalt, gold, iridium, and copper, also adsorb small quantities of hydrogen

The process of occlusion is accompanied by an evolution of heat, 4370 calories being evolved per gram of hydrogen occluded; the thermal effect is the same for each successive fraction of gas adsorbed (Favre, Compt. rend. 1869, 68, 1306; Mond, Ramsay, and Shields, *l.c.*).

The nature of the substances formed when hydrogen is occluded by metals has not yet been determined with certainty. The metals are unaltered in appearance, and such physical properties as thermal and electrical conductivity, sp.gr., and tenacity are only slightly diminished. Graham was of opinion that no chemical union occurs, but that the hydrogen assumes the solid form and acts as a quasi-metal. This adsorbed form of hydrogen he proposed to call *hydrogenium.*

From the expansion of alloys of palladium with platinum, gold, and silver, when charged with hydrogen, Graham calculated the sp.gr. of hydrogen to be 0·733; subsequent determinations by Dewar gave the figure 0·620, a figure which does not compare at all with the actual sp.gr. of solid hydrogen.

Troost and Hautefeuille (Compt. rend. 1874, 78, 686) believed that their experiments indicated the existence of a definite compound, Pd_2H, whilst Dewar (Chem. News, 1897, 76, 274) suggested the existence of Pd_3H_2. The fact that when fully charged with hydrogen, the composition of palladium-hydrogen approximates closely to this latter formula is, however, almost the only evidence that can be adduced in support of the existence of this compound (Mond, Ramsay, and Shields, *l.c.*). The experiments of Hoitsema (Zeitsch. physikal. Chem. 1895, 17, 1) have shown that between 20° and 200° no definite compounds of palladium and hydrogen exist; at constant temperature the relationship between the vapour tension of the system palladium-hydrogen and the percentage of hydrogen in the solid phase is such, however, as would be expected if two partially-miscible solid solutions of hydrogen in the metal are formed, the miscibility of which increases with rise of temperature.

According to Holt, Edgar, and Firth, the action of the palladium depends on its treatment. They conclude that the hydrogen exists partly as an adsorbed layer of high pressure removable by evacuation, and partly absorbed and distributed irregularly in the mass of the metal. In the sorption 4370 cals. per gram hydrogen are evolved and the palladium increases about 10 p.c. in volume. About 92–98 p.c. of the hydrogen is evolved at ordinary temperatures *in vacuô*, and the expulsion is complete at 440°. Under high pressure the hydrogen is retained to the extent of 300 vols. at 500°.

The specific electrical conductivity and density of palladium hydrogen alloys have been measured by Wolf (Zeitsch. physikal Chem. 1914, 87, 575). The diffusion of hydrogen through a palladium septum at temperatures ranging from 70° to 300° and at pressures between 700 and 100 mm. has been measured by Holt (Proc. Roy. Soc. 1915, [A] 91, 148). At these pressures the rate of diffusion is proportional to the pressure of the gas. At pressures below 100 mm. the diffusion is much slower, and no simple relation to the pressure can be traced. As regards platinum, platinum black, made by mixing boiling solutions of sodium chloroplatinate with sodium formate, is much more active towards hydrogen than spongy platinum, absorbing 100 vols. as against 1 vol. at 0°.

The meteoric iron of Lenarto, containing 91 p.c. of iron, yields 2·85 times its volume of occluded gas, mainly hydrogen (Graham, Proc. Roy. Soc. 1867, 15, 502). Since under ordinary pressure iron absorbs only half its volume of hydrogen, this would seem to show that the meteorite has come from an atmosphere containing hydrogen under a pressure much greater than that of our own atmosphere, thus affording a confirmation of the conclusions drawn from spectroscopic observations regarding the existence of dense and heated hydrogen atmospheres in the sun and fixed stars.

Atomic weight of hydrogen. This has been determined by measuring the ratio of the combining weights of oxygen and hydrogen. Since this ratio is of fundamental importance, a very considerable amount of attention has been directed towards its accurate measurement. The methods used may be grouped under two headings: (*a*) synthesis of water; and (*b*) determinations of the relative densities of hydrogen and oxygen.

(*a*) The classical method, first employed by Dulong and Berzelius (1820), and used later by Dumas (Ann. Chim. Phys. 1843, [iii.] 8, 189) in his elaborate series of determinations, consists in reducing heated cupric oxide in a stream of pure, dry hydrogen, and estimating the water produced and the loss in weight experienced by the cupric oxide. The result obtained by Dumas, viz. H : O :: 1 : 15·9607, corroborated as it was by the experiments of Erdmann and Marchand (J. pr. Chem. 1842, 26, 461) was for many years accepted as the true value; but subsequent work has shown that this result deviates considerably from the truth, and has disclosed numerous sources of error in the older determinations. The method of Dumas, with various modifications, has been used by Cooke and Richards (Amer. Chem. J. 1888, 10, 81, 191); Keiser (*ibid.* 1888, 10, 249); Noyes (*ibid.* 1889, 11, 155; 1890, 12, 441); Dittmar and Henderson (Proc. Roy. Soc. Glasgow, 1891, 22, 33), and Leduc (Compt. rend. 1892, 115, 41); their results are given in the table below.

The synthesis of water has been effected by other methods than the above. In 1889, Rayleigh (Proc. Roy. Soc. 45, 425) weighed pure hydrogen and oxygen in glass globes, mixed them and then gradually exploded the mixture in a eudiometer. The residual gas was then analysed, and hence the ratio of hydrogen to oxygen determined. The first complete quantitative synthesis of water in which both gases were weighed separately, and afterwards in combination, is due to Morley (Smithsonian Contributions to Knowledge, 1895, 29). The hydrogen was weighed in palladium (a method due to Keiser) and the oxygen in compensated globes, after the manner of Regnault. After weighing, the gases were burned by means of electric sparks in a suitable apparatus, from which the unburned residue could be withdrawn for examination. Finally, the apparatus containing the water produced was closed by fusion and weighed.

The syntheses of water by Keiser (Amer. Chem. J. 1898, 20, 733) were effected by the direct oxidation of hydrogen occluded in palladium; the hydrogen, oxygen, and water were all determined. The experiments recorded in the elaborate investigation by Noyes (J. Amer. Chem. Soc. 1907, 29, 1718) were performed partly by this method and partly by the method employed in his earlier work (*v. supra*). A novel, but indirect method for measuring the ratio of oxygen to hydrogen has been employed by Thomsen (Zeitsch. anorg. Chem. 1895, 11, 14).

The results of these experiments are collected in the following table:—

Experimenter	Date	Ratio O/H	At. wt. of Hyd. (O = 16)
Dumas . . .	1842	15·9607	1·00246
Erdmann & Marchand	1842	15·9750	1·00156
Cooke & Richards .	1887	15·8690	1·00825
Keiser . . .	1888	15·9514	1·00305
Noyes . . .	1889	15·8966	1·00650
Dittmar & Henderson	1891	15·8677	1·00834
Leduc . . .	1892	15·8810	1·00750
Rayleigh . . .	1889	15·8900	1·00692
Morley . . .	1895	15·8790	1·00762
Keiser . . .	1898	15·8799	1·00756
Noyes . . .	1907	15·8745	1·00783
Thomsen . . .	1895	15·8690	1·00825

The weighted mean of these results is H = 1·00769 according to Clarke (A Recalculation of the Atomic Weights, 3rd edit. 1910, 29, 4th edit. 1920).

(*b*) The ratio of the densities of oxygen and hydrogen is, subject to a correction to be mentioned later, equal to the ratio of their atomic weights. The first accurate measurements of these densities were made by Dumas and Boussingault in 1841 (Compt. rend. 12, 1005); the results obtained four years later by Regnault (*ibid.* 20, 975) were adopted as standard values for many years, and gave for the ratio a value of 15·9611. The remarkable agreement of this figure with that deduced from Dumas' synthesis of water is only, however, accidental, for in 1885, Agamennone, and independently, Rayleigh in 1888 (Proc. Roy. Soc. 43, 356) pointed out a serious error in all previous determinations of gaseous densities, owing to the fact that the glass globes in which the gases are weighed are elastic, and shrink to a measurable extent when evacuated. The effect of neglecting to correct for this shrinkage is that the apparent weight of gas is slightly lower than its true value. The corrected value for the density ratio from Regnault's experiments is 15·9105 (Crafts, Compt. rend. 1888, 106, 1662).

The densities of hydrogen and oxygen have been frequently determined with the utmost care; *v.* Rayleigh (Proc. Roy. Soc. 1892, 50, 448); Cooke (Amer. Chem. J. 1889, 11, 509); Leduc (Compt. rend. 1891, 113, 186); Thomsen (Zeitsch. anorg. Chem. 1896, 12, 4) and especially Morley (Smithsonian Contributions, 1895). The table below summarises the results obtained :—

Experimenter	Date	Density ratio O/H
Dumas & Boussingault .	1841	15·9015
Regnault . . .	1845	15·9105
Rayleigh . . .	1888	15·8840
Rayleigh . . .	1892	15·8820
Cooke	1889	15·8900
Leduc	1891	15·9060
Morley . . .	1895	15·8955
Thomsen . . .	1896	15·8878

The weighted mean is 15·8948 (Clarke, *l.c.*)

This result is subject to a slight correction for the fact that hydrogen and oxygen do not combine together by volume exactly in the ratio of two to one; according to Morley (*l.c.*), the exact ratio is 2·00274 (*cf.* Scott, Phil. Trans. 1893, 184, 543; Leduc, Compt. rend. 1892, 175, 311; Rayleigh, Proc. Roy. Soc. 1904, 73, 153). Correcting the above mean value for the density ratio, in accordance with this result, the figure 15·8726 is obtained, which leads to the value 1·00803 for the atomic weight of hydrogen on the oxygen scale.

Determinations of the volumetric composition of water by Burt and Edgar (Phil. Trans. 1916, [A] 216, 393) gave the volume ratios of H to O as 2·00288 : 1. From this value, taking the normal litre weights of oxygen and hydrogen as 1·42900 and 0·089873 gram respectively the atomic weight of hydrogen becomes 1·00772.

According to Clarke (*l.c.*), the probable mean derived from the results of methods (*a*) and (*b*) combined, is H=1·00772. A review of the most trustworthy results of the various determinations which have been made since the time of Berzelius leads Hinrichs (Rev. gen. Chim. pure Appl. 1910, 13, 351) to consider 1·0078 as the most probable value. The value at present adopted is H=1·0077.

Applications of hydrogen. Hydrogen is used in conjunction with oxygen for the production of the Drummond or oxy-hydrogen lime light. For this purpose, the gases are compressed in iron bottles furnished with taps and jets, so that they can be allowed to escape, and burned as required. They are allowed to impinge on a cylinder of lime which is thereby heated to whiteness, and gives a light almost equal to the electric arc.

For the autogenous welding of metals, the working of platinum, and the manufacture of laboratory utensils and mercury vapour lamps from fused quartz, hydrogen in the form of the oxyhydrogen blowpipe flame is used in large quantities, although it has here to meet the competition of acetylene, which is cheaper and readily obtainable as required from calcium carbide, requires less gas, and yields a higher temperature.

Autogenous soldering.—This process is much used for uniting the edges of the sheets of lead which are employed in making vessels for the purpose of holding acids. Joints made in this way are much more durable than those made with solder. The apparatus for this purpose is made so that hydrogen can be generated at pleasure, and when not in use the pressure of gas inside the apparatus lifts the acid out of contact with the zinc. The hydrogen generator consists of a cylindrical copper vessel lined with lead; there is an upper and lower chamber connected by a pipe, and they are fitted with arrangements which admit of easy renewal of acid or zinc and the removal of the zinc sulphate formed. The apparatus gives a very constant flame, which may be used with advantage in soldering lead in the way which is practised in the construction of sulphuric acid chambers. The hydrogen is delivered from a platinum-tipped nozzle through which a jet of air also issues from a foot bellows; this is effected by attaching the nozzle by means of india-rubber tubing to a tube which branches out V-shaped into two limbs each provided with a stopcock; each of these limbs is provided with an india-rubber tube, one of which is attached to the bellows and the other to the delivery tube of the hydrogen generator. The operator can, therefore, carry the nozzle in his hand and direct the flame where he pleases, and by means of the stopcock he can readily regulate the supply of air or hydrogen.

The best proportion in which to use the gases for welding is one part of oxygen and four parts of hydrogen; if the amount of oxygen is increased the flame may oxidise the metal.

Tungsten lamps.—The manufacture of tungsten filament lamps requires a regular supply of hydrogen to prepare the inert atmosphere in which the filaments are heated to a high temperature during the final treatment. It is almost the universal custom to employ a mixture of equal volumes of hydrogen and nitrogen when the filaments are electrically heated to whiteness. Since incandescent tungsten filaments are very sensitive to oxidation, it is of great importance that the hydrogen employed should be of a high degree of purity. The process devised by Lane (*v. infra*) is frequently adopted for obtaining the gas, since besides preparing hydrogen, it also admits of nitrogen being collected.

Hydrogen for balloons.—After the publication by Cavendish of his researches on 'inflammable air,' Charles, in 1783, suggested the use of hydrogen for the inflation of balloons. Montgolfier had, during the same year, invented the balloon which he inflated with rarefied air.

In hydrogen, however, Charles recognised a much more suitable means of inflation, although the cost was very considerable, 500 lbs. of sulphuric acid and twice that amount of iron being consumed in the inflation of a balloon about 13 feet in diameter. A military airship of 250,000 cubic feet capacity would require about 18 tons of iron and 31 tons of sulphuric acid.

The first balloon sent up from English soil, on Nov. 25, 1793, was inflated with hydrogen. In the following year, the French Government instituted a series of experiments at Meudon under Guyton de Morveau, Contelle, and Comté, with the view of perfecting the balloon for reconnoitring, signalling, and other warlike purposes. For the preparation of the hydrogen, Guyton de Morveau suggested a method invented by Lavoisier, that of passing steam over red-hot iron, and a furnace was accordingly built, which after many trials, was capable of producing sufficient gas to fill a balloon, 27 feet in diameter, in 4 hours. This balloon, with one filling, remained in use for a month.

Balloons inflated with hydrogen were used in the American Civil War in 1861. The gas was generated from old scrap iron and sulphuric acid in wooden tanks lined with lead; the apparatus was carried from place to place on two carts.

In 1878, Giffard made a gigantic captive balloon for the Paris Exhibition. It was spherical in form, 118 feet in diameter, and had a capacity of 882,902 cub. feet. To fill this great aerial ship with hydrogen gas, 190 tons of sulphuric acid and 80 tons of iron were consumed (Jour. United Service Inst. 27, 735–756).

Hydrogen was also used in the Soudan War for inflating balloons. For this purpose, the gas was compressed in strong iron cylinders, 12 feet long by 1 foot in diameter; these were for a reserve supply, and weighed half a ton each. A gas factory and pumping station were put up. To meet first requirements about 100 lighter cylinders, 9 feet long, and containing 120 feet of gas in a compressed condition, were taken out; these were so constructed as to be easily carried by men. One waggon containing a ton of stores was sufficient for a balloon ascent; a volume of gas occupying 4,150 feet was sufficient to lift a man 1,000 yards (Illus. Nav. and Mil. Gaz. 11, 172).

At the present time it is highly important for the maintenance of large dirigible balloons to be assured of a regular supply of pure hydrogen gas. Minute quantities of impurities, such as phosphine and arsine attack the fabric of the balloon. The chief drawback to the use of hydrogen is its high rate of diffusion, a drawback which is being minimised by improvements in the manufacture of balloon fabrics.

Most of the hydrogen now used for inflating the gas bags of dirigible airships is produced either electrolytically or by the action of steam on red-hot iron. The former method depends for success upon a cheap supply of electrical energy. It yields pure hydrogen and the plant requires very little attention.

In the other method as described by Lane (Eng. Pat. 17591, 1909), iron is heated to redness in a current of steam, and the oxide produced is reduced by heating in a current of water-gas, the resulting metal being used again. By carrying on the reduction process in a number of the retorts and the preparation of hydrogen simultaneously in the others, it is possible to make the production of hydrogen more or less continuous.

The need for rapid convenient methods for preparing hydrogen for military purposes has led to the introduction of the '*silicol*,' '*hydrolith*,' and '*hydrogenite*' processes for its preparation. These are due to Jaubert, and are employed by the French army. In the 'silicol' process ferrosilicon containing 88–90 p.c. or more of silicon is acted upon by a 35–40 p.c. solution of caustic soda at 60°–80°. The heat of the freshly-prepared solution is sufficient to start and maintain the reaction. This method was employed by the British navy during the recent war. According to Weaver (J. Ind. Eng. Chem. 1920, 12, 232) the process yields the most economical results when about equal weights of sodium hydroxide (as 30 p.c. solution) and ferrosilicon (88 p.c. Si) are used. For a charge of 363 kg. of ferrosilicon, one half of the sodium hydroxide solution and 28 kg. of ferrosilicon are placed in the generator (a cylindrical tank 6 ft. 6 in. high and 6 ft. diameter), and when the temperature reaches 90°, ferrosilicon is added at the rate of 5·8 kg. per minute; sodium hydroxide is at the same time added continuously at such a rate that the temperature remains constant. When all the solution has been added, the temperature is kept at 90° by the introduction of cold water until the solution contains about 20 p.c. sodium hydroxide (J. Soc. Chem. Ind. 1920, 39, 403 A). In the 'hydrolith' process, a white crystalline powder consisting of calcium hydride (90 p.c. pure, the remainder being oxide and nitride), is decomposed by water. One kilo. of the solid yields about 1 cubic metre of hydrogen. The portable apparatus used by the French army can fill an army dirigible in 4 hours. For speed, convenience, and reliability, hydrolith is unexcelled, but its high cost renders its use almost prohibitive for private aeronautics. 'Hydrogenite' is a compressible powder, consisting of ferrosilicon (90–95 p.c. Si) 25 pts., sodium hydroxide 60 pts., and soda lime 20 pts. (Sander, Chem. Zeit. 1911, 35, 1273): when ignited by a suitable 'match,' it reacts spontaneously, much as do thermit mixtures, with the evolution of hydrogen and the production of sodium and calcium silicates. The material is hygroscopic, and is sold in a compressed cake in metal cartridges. One kilo. of substance yields from 270 to 370 litres of hydrogen. (For the method of using the substance for filling balloons, *v.* Jaubert, Rev. gén. chim. 13, 341, 357; and *cf.* D. R. P. 218257, 1908.)

Hydrogen in chemical industry. Hydrogen for commercial purposes may be obtained electrolytically, or by purely chemical methods, as in the iron contact process, whereby purified 'blue' water-gas, a mixture containing hydrogen and carbon monoxide, obtained by passing steam over heated coke (*v.* WATER-GAS) is passed, alternatively with steam, over iron oxide, the oxide being continually reduced and oxidised, with the production of hydrogen and carbon dioxide, which latter gas is removed by washing and absorption; or as in the Badische catalytic process, where the purified 'blue' water-gas is mixed with steam and passed over some catalytic material (as a preparation of a nickel, iron, or chromium salt) dried and heated to 400°–500°, when the mixture of hydrogen and carbon monoxide reacts with the steam with the formation of more hydrogen and carbon dioxide:

$$\underset{\text{Water-gas.}}{H_2+CO}+\underset{\text{Steam.}}{H_2O}=2H_2+\underset{\text{Carbon dioxide.}}{CO_2}$$

The mixture of hydrogen and carbon dioxide is passed under pressure through water whereby the carbon dioxide is absorbed. Or the purified 'blue' water-gas may be subjected to a regulated cold and pressure, as in the Linde-Frank-Caro process, whereby all its components, with the exception of the hydrogen, may be removed by liquefaction (*cf.* E. K. Rideal, J. Soc. Chem. Ind. 1921, 40, 10T.). Hydrogen is now required on a large scale for the hardening of fats and oils (*q.v.*) and for the production of synthetic ammonia (*v.* AMMONIA; CHEMICAL AFFINITY; UTILISATION OF ATMOSPHERIC NITROGEN).

Triatomic hydrogen (*hyzone*). A reactive modification of hydrogen has been produced by several methods, all of which are dependent on gaseous ionisation: (i) by the α-rays from radium emanation; (ii) by an electrical discharge under reduced pressure; and (iii) by the high potential corona at atmospheric pressure. This active hydrogen reduces sulphur, arsenic, phosphorus, mercury, nitrogen, and both acid and alkaline solutions of potassium permanganate. It is condensed or destroyed by temperatures about that of liquid air. It is very unstable and reverts to the ordinary form in about a minute. The formation of a polyatomic molecule is indicated by the contraction of the hydrogen when ionised. Positive ray analysis at very low pressures shows a large proportion of triatomic molecules responsible for the chemical activity. All the properties of the gas point to its being an ozone form (Wendt and Landauer, J. Amer. Chem. Soc. 1920, 42, 930; Chem. Soc. Abstr. 1920, 118, ii. 425).

HYDROGENIUM *v.* HYDROGEN.

HYDROGEN PEROXIDE. Symbol H_2O_2. This compound was discovered in 1818 by Thenard. It occurs at times in small quantities in the atmosphere, in dew, in rain, and in snow (Schöne, Ber. 1874, 7, 1695; *ibid.* 1893, 26, 3011; *ibid.* 1894, 27, 1233; Zeitsch. anal. Chem. 1894, 33, 137): but Ilosva (Ber. 1894, 27, 920) maintains that the tests used for detecting it in these media would also be given by the oxides of nitrogen, which are always present. It is said to be contained in many green plants (Bach. Compt. rend. 1894. 119, 1218; Chodat and Bach, Ber. 1902, 35, 1275, 3943; 1903, 36, 1756; 1904, 37, 36). It is also contained in solution in the water produced by the combustion of hydrogen in oxygen (Schuller and Bach, Compt. rend. 1897, 124, 951; Keiser and McMaster, Amer. Chem. J. 1908, 39, 96), and in the flames of alcohol, coal gas, ether, and carbon disulphide (Engler, Ber. 1900, 33, 1109).

Water in contact with oxygen yields hydrogen peroxide on exposure to sunlight. When air at atmospheric pressure is led through the cathode compartment of an electrolytic cell containing 1 p.c. sulphuric acid hydrogen peroxide is formed at the cathode. With oxygen the amount is increased and is also increased by increasing the pressure of the oxygen. Working with a potential of 2 volts, a current density of 2 amps. per sq. dcm. and a pressure of 100 atmos., a 2·7 p.c. peroxide solution can be obtained. 300–400 grams of hydrogen peroxide can be obtained for each kilowatt-hour.

Hydrogen peroxide is formed in small quantities in the electrolysis of aqueous solutions (Richarz, Zeitsch. anorg. Chem. 1903, 37, 75; Ber. 1909, 42, 4674; Riesenfeld and Reinhold, *ibid.* 2977); when a Tesla brush discharge, or the silent electric discharge is passed through water vapour (Findlay, Zeitsch. Elektrochem. 1906, 12, 129; Nernst, *ibid.* 1905, 11, 710; Löb, Ber. 1908, 41, 1517; Ringe and Fischer, *ibid.* 945); during the slow oxidation of many metals, particularly their amalgams, in the presence of water (Traube, Ber. 1893, 36, 1471; Smith, Chem. Soc. Trans. 1906, 481; Barnes and Shearer, J. Phys. Chem. 1908, 12, 155, 468; Rankin, Proc. Roy. Soc. 1910, B, 82, 78); with zinc amalgam and in the presence of an alkaline earth a better yield is said to be obtained (D. R. P. 48542; J. Soc. Chem. Ind. 1890, 213).

It may be synthesised by the action of the silent electric discharge upon oxy-hydrogen gas cooled by liquid air under a pressure of [illegible] cm. of mercury (Fischer and Wolf, Ber. 1911, 44, 2956). A mixture of hydrogen and oxygen containing oxygen up to 6 p.c. on being subjected to a silent discharge in a Berthelot tube produced large quantities of hydrogen peroxide, the yield in some cases being practically 100 p.c. The best yield was obtained under the following conditions: (1) a current strength of 4·6 amps. on the primary of the induction coil; (2) a gas velocity of 400 c.c. per hour; (3) moist gases; (4) a concentration of 3·5 p.c. oxygen (Wolf, Zeitsch. Elektrochem. 1914, 20, 204).

Hydrogen peroxide is also formed under several other circumstances, as, *e.g.*, when freshly-ignited bone black is moistened with as much water as it will take up, and exposed to light and air. Even in a few minutes a perceptible amount of hydrogen perioxide is formed (Dingl. poly. J. 256–519). A carbonic oxide flame (when the gas has been previously passed through water) is said to produce it in quantity, or if burnt in contact with the surface of water the same effect is produced (J. Soc. Chem. Ind. 1884, 496).

When turpentine oil or any other hydrocarbon containing a terpene is oxidised by air or ozone in the presence of water, hydrogen peroxide is formed and passes into solution in the water. In this way it is possible to prepare a solution of two volumes strength, that is to say, of such a strength that when fully decomposed it is capable of yielding twice its own volume of oxygen gas (Kingzett, Eng. Pat. 12274; J. Soc. Chem. Ind. 1898, 691).

It is also said to be produced by the oxidation of a number of organic compounds, such as urine, ether, &c., in direct sunlight (Richardson, Chem. Soc. Trans. 1893, 1110; *ibid.* 1896, 1349).

Preparation.—1. By passing a copious stream of well-washed carbon dioxide through cooled distilled water to which is added very gradually pure barium peroxide, finely powdered and suspended in water. The cautious addition of the barium peroxide is necessary, as an excess of it would cause the decomposition of any hydrogen peroxide formed, with evolution of oxygen and formation of water. After allowing the gas to pass some considerable time, the barium carbonate is filtered off, and the solution evaporated *in vacuó* over sulphuric acid until it acquires a syrupy consistency;

$$BaO_2+CO_2+H_2O=H_2O_2+BaCO_3$$

(D. R. P. 179771, 179826; J. Soc. Chem. Ind 1906, 117).

2. The preparation is also effected by the decomposition of barium peroxide with hydrofluoric, silicofluoric, phosphoric, sulphuric, borofluoric, or hydrochloric acid, of which the last is to be preferred, owing to its cheapness, whilst the purest peroxide is obtained with phosphoric or borofluoric acids. The barium peroxide, which must be of the purest quality and very finely ground, is made into a thin paste with water, and introduced very gradually into the acid solution, the temperature of which must never exceed 10°–15°, and must be constantly agitated. When the solution is nearly neutralised, the liquid is decanted from the precipitate, and freed from iron and aluminium oxides by treatment with sodium phosphate solution, then with sufficient barium peroxide or waste barium oxide to make the liquid neutral, lastly with ammonia, after which it is rapidly pumped through a filter press. It is then freed from dissolved baryta by the addition of sodium sulphate. The most stable peroxide is that prepared with phosphoric acid, and contains a small amount of that acid in the free state (Chem. Zeit. 9, 949 and 976; Bourgougnon, J. Amer. Chem. Soc. 12, 64; Fawsitt, J. Soc. Chem. Ind. 1902, 229; *see* also Eng. Pats. 10476, 3628, 21333; J. Soc. Chem. Ind. 1891, 482; *ibid.* 1892, 707; *ibid.* 1900, 70). Nitric acid has also been employed (Fr. Pat. 359523; J. Soc. Chem. Ind. 1906, 374).

3. Hydrogen peroxide has also been conveniently, but not so cheaply, prepared by treating sodium peroxide with hydrofluoric or hydrochloric acids (U.S. Pat. 692139; J. Soc. Chem. Ind. 1902, 364; Forcrand, Compt. rend. 1899, 129, 1246; Merck, Chem. Zentr. 1904, ii. 67); and by treating persulphates, percarbonates, and perborates, obtained by electrolysis of the ordinary acids with dilute acids (Jaubert, Chem. Zentr. 1905, ii. 99; D. R. PP. 217538, 217539, 195351, 199958, 179826; J. Soc. Chem. Ind. 1905, 379; *ibid.* 1906, 321, 379; *ibid.* 1908, 448, 856; *ibid.* 1910, 489).

To obtain hydrogen peroxide from persulphates, acid solutions of persulphates, obtained by electrolysis, or by treating solid persulphates with sulphuric acid, are converted on warming into monopersulphuric acid:

$$H_2S_2O_8+H_2O=H_2SO_5+H_2SO_4$$

and this into hydrogen peroxide:

$$H_2SO_5+H_2O=H_2SO_4+H_2O_2$$

The solutions must contain a high concentration of sulphuric acid (*circa* 40 p.c.) in order that $H_2S_2O_8$ may be converted into H_2SO_5. The concentration must not be too great since the action is reversible; in solutions containing over 58 p.c. H_2SO_4 the H_2O_2 reforms H_2SO_5. A certain strength of sulphuric acid is needed to obtain a concentrated distillate at a fairly rapid rate. The general conditions affecting the stability of hydrogen peroxide must be observed. The solution must not contain salts of copper, iron, or manganese, and must be free from dust or organic matter. Traces of platinum derived from the electrodes catalyse the decomposition of H_2O_2 in presence of H_2SO_5

$$H_2SO_5+H_2O_2=H_2SO_4+H_2O+O_2$$

Teuchner (Eng. Pat. 24507, 1905) removes these traces of platinum by adding aluminium, the salts of which have no catalytic influence. For the most successful conditions of distillation, *see* Pietzsch and Adolph, Eng. Pats. 23158 and 23660.

Persulphates (of potassium and ammonium) are distilled with sulphuric acid, giving H_2O_2 of high concentration:

$$K_2S_2O_8+H_2SO_4=K_2S_2O_7+H_2SO_5$$
$$H_2SO_5+H_2O=H_2O_2+H_2SO_4$$

Water is introduced and the H_2O_2 is distilled as fast as formed at a high concentration. By this means 96 p.c. of the theoretical yield of H_2O_2 from $K_2S_2O_8$ may be obtained as a 20 p.c. solution. On the large scale 1 kilo. of ammonium persulphate is said to be produced by 2·4 kilowatt-hour. Assuming 96 p.c. efficiency of conversion into H_2O_2 and distillation as above, 1 kilowatt-hour produces about 60 grams H_2O_2 (Prideaux, J. Soc. Chem. Ind. 1918, 257 R).

Hydrogen peroxide is produced by Cobellis (U.S. Pat. 1195560) by heating a solution of ammonium persulphate and bisulphate. The process is made continuous by electrolysing a solution of ammonium sulphate at comparatively low temperatures to form the per-salt, heating under pressure to form sulphate and hydrogen peroxide which is subsequently distilled off under diminished pressure in a current of inert gas (Reports of the Progress of Applied Chemistry, 1917, ii. 192).

Pure concentrated solutions of hydrogen peroxide have been prepared by the action of alcohol and dilute sulphuric acid on sodium peroxide in earthenware, glass, or lead vessels at −10°. The alcohol is then removed by distillation *in vacuó* (Dony-Hénault, Fr. Pat. 403294; J. Soc. Chem. Ind. 1909, 1314). A mixture of a perborate with an equivalent amount of a dry solid organic or inorganic acid, or of a solid acid salt has been prepared, which, on treatment with water, yields hydrogen peroxide (Fr. Pat. 401911; J. Soc. Chem. Ind. 1909, 1198).

Hydrogen peroxide has also been prepared by blowing superheated steam against a heated body (Eng. Pat. 20868, 1907; Fr. Pat. 382189, 1907; D. R. P. 205262, 1908; J. Soc. Chem. Ind. 1906, 808; *ibid.* 1908, 123, 226; *ibid.* 1909, 140; Fischer and Ringe, Ber. 1908, 41 945), and by blowing moist air against a spark or arc discharge (D. R. PP. 197023; 228425; J. Soc. Chem. Ind. 1910, 1462).

(For other methods, *see* D. R. P. 185597; Bornemann, Zeitsch. anorg. Chem. 34, 1; Fr. Pat. 371043; Scheuer and Vernet, Bull. Soc. Ind. Mulhouse, 1907, 77, 336; *ibid.* 1908, 78, 184, 187; J. Soc. Chem. Ind. 1910, 1306; Fr. Pat. 415361; Eng. Pats. 10476, 1913; 22714, 1914.)

Commercial hydrogen peroxide is liable to contain hydrochloric, sulphuric, phosphoric, and hydrofluoric acids, alumina, lime, magnesia, potash, and soda, derived from water or other materials used in its manufacture, whilst baryta and traces of iron, copper, lead, and manganese are sometimes found if it has been carelessly made.

When these last are present, the product is tolerably stable only if it be sufficiently acid, though even then it is less stable than in the absence of these impurities.

It is usually sold as of so many volumes strength, that is, the unit volume gives 10, 12, 20 unit measures of oxygen.

The commercial liquid of so-called 10 volume or about 3 p.c. strength may be purified by the addition of about ½ p.c. of concentrated phosphoric acid (preferably pure) to precipitate iron, copper, lead, and manganese, and prevent the subsequent formation of their peroxides which would otherwise take place. Saturated baryta water (hot or cold) is then added very gradually, until neutrality is reached. No excess must be used or hydrated BaO_2 will be precipitated, which will induce decomposition of a portion of the hydrogen peroxide.

The clear liquid is now drawn off, and is poured into an excess of cold saturated baryta water, when hydrated BaO_2 is thrown down, and is then washed until no metal except barium can be detected in the washings.

The BaO_2 is then suspended in water and added drop by drop to a solution consisting of 90 parts of distilled water to 10 parts of pure concentrated sulphuric acid until only traces of acid remain free; these are best removed by weak baryta water, for an accidental excess of BaO_2 will induce decomposition of some of the already formed hydrogen peroxide, whilst an excess of BaO will have no such effect. The barium sulphate is allowed to settle, and the clear liquid drawn off, if found free from both barium and sulphuric acid. The resulting product is about 3 p.c. strength, fairly stable and of great purity (Mann, Chem. Zeit. 12, 857; J. Soc. Chem. Ind. 1889, 640).

Hydrogen peroxide does not volatilise appreciably from its aqueous solutions at 50°–60°. The most important factor in the decomposition is the purity of the water used as solvent, tap-water giving a rate which is 50 times that of the best conductivity water.

The commercial solutions can be concentrated to 95–99 p.c. by evaporating in air at 75° to 20 p.c. strength, then *in vacuô* to 50–55 p.c., after which it is treated with ether, in which the peroxide is readily soluble. The ethereal extract is then carefully distilled and fractionated *in vacuô* (Wolffenstein, Ber. 1894, 27, 3307; Staedel, Zeitsch. angew. Chem. 1902, 15, 642; Tyrer, *l.c.*; Merck, *l.c.*); also by distilling the solutions at a temperature below 85° in a powerful current of an inert gas (D. R. P. 219154).

The concentrated solution remains liquid at −20°, but when immersed in a mixture of ether and carbon dioxide, it crystallises to a solid mass, consisting of the anhydrous peroxide. Clear colourless crystals of the latter can also be obtained by introducing a fragment of the solid into a freshly prepared 90–80 p.c. solution at −8° (Staedel, *l.c.*). Hydrogen peroxide should be kept in paraffin or paraffin-lined vessels.

The decomposition of hydrogen peroxide under the influence of heat is regulated principally by the amount of water existing at each instant in the liquid, and follows a mathematical law resulting from this; thus the water acts as a catalyst. The physical state of the walls of the containing vessels has a marked influence on the results (Lemoine, Compt. rend. 1912, 155, 9; Bull. Soc. chim. 1913, 13, 5).

A number of substances have been proposed as suitable for increasing the stability of hydrogen peroxide, such as sulphuric or phosphoric acids (Tyrer, Pharm. J. 63, 100); sodium pyrophosphate (Eng. Pat. 23676; J. Soc. Chem. Ind. 1916, 151); organic substances such as alcohol, ether, glycerol, &c. (Sanders, Bull. Soc. Ind. Mulhouse, 1897, 95; Freyes, *ibid.* 97, Eng. Pat. 15993); 1 gram pure crystalline naphthalene to 1 litre of solution (Zinno, Bull. Soc. Ind. Mulhouse, 1895, 78); gallic acid or pyrogallol (Arndt, D. R. P. 196370); uric or barbituric acids (D. R. PP. 216263, 203019, J. Soc. Chem. Ind. 1908, 1204; *ibid.* 1909, 1314); phenacetin or an amide or imide or acetyl derivative of an aromatic base (J. Soc. Chem. Ind. 1906, 1219); oxalic acid (Fischer, Pharm. Zentr. 1907, 48, 57, 79); *p*-acetylaminophenol (Schlangk, Apoth. Zeit. 1911, 26, 106).

Acetanilide has been found to be fairly efficient as a preservative. Benzoic and salicylic acids have also been recommended.

According to Allain (J. Pharm. Chim. 1906, 24, 162) sodium or calcium chloride in the proportion of 1 p.c. are more efficient preservatives for medicinal hydrogen peroxide than sulphuric or phosphoric acids. They are also less objectionable than the latter from a therapeutic point of view. *See* also Kingzett (J. Soc. Chem. Ind. 1890, 3).

Clover (Amer. J. Pharm. 1913, 85, 538) has studied the influence of various acids and salts on the gradual decomposition of hydrogen peroxide solutions. Addition of salts of the alkali and alkaline-earth metals does not appear to have any marked effect. Of the acids used, phosphoric acid gave the best result at all concentrations, but the best preserved solution had lost nearly 30 p.c. in strength after seven months. Traces of copper and iron have a very deteriorating effect, but this is prevented to a great extent by acetanilide.

According to Merck (D. R. P. 275499) the stability of solutions of hydrogen peroxide, or its solid compounds with carbamide, ammonium sulphate, &c., can be greatly increased, without rendering the mixture acid by the addition of acyl derivatives of aminohydroxycarboxylic acids. The solution should react acid to dimethyl yellow and should be kept in brown glass bottles (*cf.* Jensen, Pharm. J. 1920, 87).

The amount of hydrogen peroxide in an aqueous solution may be conveniently determined by titration with a solution of potassium permanganate containing 7·9 grams $KMnO_4$ per litre. 2 c.c. of hydrogen peroxide solution are introduced into a graduated tube of 35 c.c. capacity, 5 or 6 drops of hydrochloric acid are added, and then the solution of permanganate is gradually introduced with constant agitation until the contents of the tube are of a red or brownish colour; the quantity of solution is then read off, 5 c.c. representing 1 p.c. of hydrogen peroxide. The results are accurate to within 0·1 p.c. and can be obtained in a few minutes[1] (Chem. Zeit. 9, 940 and 976).

In the presence of persulphates, however, accurate results can only be obtained by using a minimum volume of solution, a large excess of sulphuric acid and performing the titration very rapidly; for this purpose an excess of permanganate is added, and the latter is then titrated back with sodium thiosulphate (Friend, Chem. Soc. Trans. 1904, 597, 1533; *ibid* 1905, 1367; Skrabal and Vacek, Chem. Zeit. 1910, 34; Rep. 121).

If oxalic acid is present, this must first be removed (Sisley, J. Soc. Chem. Ind. 1901, 1028; *ibid.* 1904, 685; Roche, *ibid.* 1902, 190).

Another and more accurate method is to strongly acidify the solution of hydrogen peroxide with sulphuric or hydrochloric acid, then add a solution of potassium iodide free from iodate, and determine the iodine liberated by means of a standard solution of sodium thiosulphate (Kingzett, Chem Soc. Trans. December, 1880, and The Analyst, 1888, 13, 62; Rupp, Arch. Pharm. 238, 156; Planés, J. Pharm. Chim. 1904, 20, 538; *cf.* Auger, Compt. rend. 1911, 152, 712).

Hydrogen peroxide can also be estimated by titrating against ferrous ammonium sulphate in presence of ammonium sulphate and phosphoric acid (Mathewson and Calvin, Amer. Chem. J. 1906, 36, 113); and by estimating the quantity of arsenious acid it will oxidise to arsenic acid (Grützner, Arch. Pharm. 237, 705; Jamieson. Amer. J. Sci. 1917, 44, 150).

According to Dehn the most rapid, convenient, and accurate method of estimating hydrogen peroxide is to measure the volume of oxygen evolved when a known quantity of the solution is treated with sodium hypobromite in a special apparatus described by him (J. Amer. Chem. Soc. 1907, 29, 1315). The following reaction takes place $H_2O_2 + NaBrO = NaBr + H_2O + O_2$. By this method the presence of preservatives may be neglected. (For the estimation of the peroxide retained by fabrics, *see* Scheuer and Vernot, *l.c.*)

To determine the quantity of acid present in commercial hydrogen peroxide, the best method is by direct titration in the cold, with N/10 sodium hydroxide solution, using phenolphthalein as indicator (Brown, J. Ind. Eng. Chem. 1910, 377; Endemann. Zeitsch. angew. Chem. 1909, 22, 673; Lüning, *ibid.* 1549).

Properties.—Pure anhydrous hydrogen peroxide forms colourless prismatic crystals of sp.gr. 1·644, latent heat of fusion 74 cals., specific heat of solid 0·470; m.p. −2°, b.p. 84°–85°/68 mm., 69·2°/26 mm. It forms a syrupy transparent acid liquid, which is colourless in thin layers, but bluish-green when viewed in bulk (Spring, Chem. Zentr. 1895, i. 1105). It has sp.gr. 1·4584 at 0° (Brühl, Ber. 1895, 28, 2854); 1·4633 at 0° (Maass and Hatcher, J. Amer. Chem. Soc. 1920, 42, 2548); mean coefficient of expansion −10° to +20°, 0·00107; specific heat of liquid 0·579. It is quite stable if kept at 0°. It forms hydrates H_2O_2,H_2O; $H_2O_2,2H_2O$ (Wolffenstein, *l.c.* 3311); m.p. −51° (Maass and Herzberg, J. Amer. Chem. Soc. 1920, 42, 2560).

When heated to the boiling-point of water it decomposes with explosive violence into oxygen and water, but when the peroxide or its solutions are quite pure it is not so readily decomposed by heat; the vapours of hydrogen peroxide are said to be quite stable (Wolffenstein Ber. 1894, 27, 3307; Nernst, Zeitsch. physikal. Chem. 1904, 46, 720).

The liquid evaporates slowly *in vacuô* without the residue undergoing any change (Thenard). It bleaches organic colouring matters, but not so quickly as chlorine; when brought in contact with the skin it forms a white blister, which, after a time, produces an irritable, itching sensation (Wolffenstein, *l.c.*). It is almost insoluble in anhydrous ether, but dissolves many salts and attacks glass. Most metals cause decomposition of the pure substance, but not always explosively.

One volume of the concentrated solution yields at 14° and 760 mm. pressure, 475 volumes of oxygen, the theoretical amount being 501·8 volumes (Thenard). The compound is most stable in dilute aqueous solution; when the solution is subjected to great cold, part of the water freezes out.

The hydrogen atoms of hydrogen peroxide may be replaced by metals or acid radicles yielding derivatives which resemble the corresponding compounds of water in constitution and properties. *See* D'Ans and Friederich, Zeitsch. anorg. Chem. 1912, 73, 325.

Hydrogen peroxide is a remarkable oxidising agent. It converts arsenious into arsenic acid, and sulphurous acid into sulphuric acid; lead and other sulphides into the corresponding sulphate; manganese monoxide into dioxide, and monoxides of iron and cobalt into the sesquioxides. The monoxides of barium, strontium, and calcium are converted by it into their respective peroxides. The concentrated solution of hydrogen peroxide acts with violence on selenium, arsenic, molybdenum, and chromium, converting them at once into their oxides.

It decomposes alkaline copper, silver, and bismuth nitrate solution with evolution of oxygen and formation of the metallic oxide, or in the last case the hydroxide (Berthelot, Compt. rend. 1901, 132, 897; Moser, Zeitsch. anorg. Chem. 1906, 50, 33; Gutbier and Bünz. Chem. Zentr. 1909, i. 732.). In contact with sodium it explodes violently.

Hydrogen peroxide oxidises organic sulphides into sulphoxides (Gazdar and Smiles, Chem. Soc. Trans. 1908, 1833). It also reacts with benzene in presence of ferrous sulphate, forming phenol (Young, Chem. Soc. Proc. 1899, 131), and with α-diketones, and generally with substances possessing a quinonoid structure, and can therefore be employed for oxidising phenolic substances like brazilein and aurin, without having to protect the hydroxyl group by methylation (Perkin, Chem. Soc. Proc. 1907, 166). Hydrogen peroxide reacts with a number of opium alkaloids forming crystalline bases (Freund and Speyer, Pharm. Zeit. 1907, 52, 115). According to Schaer (Arch. Pharm. 1910, 248, 458), it may be used as a test for other alkaloids. A few milligrams of the alkaloid to be tested are added to a cooled mixture of the peroxide and sulphuric acid. Quinine gives a lemon or canary yellow colour; berberine a cherry red; hydrastine a chocolate; emetine a dark orange, and nicotine a blood-red colour.

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[1] The reaction between hydrogen peroxide and potassium permanganate in acid solution may be utilised for preparing oxygen gas. In this way a good stream of tolerably pure oxygen may be readily prepared. Crystals of the $KMnO_4$ should be placed in a Woulff's bottle containing 1 : 9 sulphuric acid, and the 8 p.c. solution of H_2O_2 allowed to drop regularly into the solution from a suitable reservoir.

In presence of ferrous sulphate hydrogen peroxide also reacts with a number of sugars, forming osones (Cross, Bevan, and Smith, Chem. Soc. Trans. 1898, 403; Morell and Bellars, *ibid.* 1905, 280; Chem. Soc. Proc. 1902, 55; Chem. News, 1904, 90, 158). It also reacts with other organic compounds (Cross, Bevan, and Heiberg, Chem. Soc. Proc. 1899, 130; Harden, *ibid.* 158; Wolffenstein, Ber. 1895, 28, 1459; Bevan and Heiberg, *ibid.* 1900, 33, 2015; Clover and Haughton, Amer. Chem. J. 1904, 32, 43).

Pure hydrogen peroxide reacts with potassium cyanide thus:

$$KCN+H_2O_2=KCNO+H_2O$$
$$KCNO+2H_2O=K(NH_4)CO_3$$

Potassium formate and ammonia are also produced, but if the peroxide contains acid, then oxamide is formed (Masson, Chem. Soc. Trans. 1907, 1449).

Chromic acid decomposes hydrogen peroxide in accordance with the equation:

$$4H_2Cr_2O_7+7H_2O_2=Cr_2(Cr_2O_7)_3+11H_2O+5O_2$$

With potassium persulphate it reacts thus:

$$H_2O_2+K_2S_2O_8=2KHSO_4+O_2$$

an unstable intermediate compound is also formed (Friend, Chem. Soc. Trans. 1906, 1092).

With sodium thiosulphate it gives the reaction:

$$3Na_2S_2O_3+4H_2O_2=2Na_2S_3O_6+2NaOH+3H_2O$$
$$Na_2S_2O_3+2NaOH+4H_2O_2=2Na_2SO_4+5H_2O$$

(Willstätter, Ber. 1903, 36, 1831).

In presence of certain solid substances, especially when finely divided, hydrogen peroxide undergoes violent decomposition, the substances themselves remaining unchanged (Fillippi, Chem. Zentr. 1907, ii. 1890; Antropoff, Zeitsch. physikal. Chem. 1908, 62, 513; Bredig and Wilkie Biochem. Zeitsch. 1908, ii. 67). This is the case with carbon, many metals, and oxides, and iodine (Walton, Zeitsch. physikal. Chem. 1904, 47, 185; Abel, Zeitsch. Elektrochem. 1908, 14, 589). Gold, platinum, and particularly silver, act most violently and evolve great heat. The presence of acids retards this decomposition, whilst the presence of alkalis facilitates it.

This decomposition is still more readily brought about by these metals, when in the colloidal state (Bredig and Reinders, Chem. Zentr. 1901, ii. 87; Bredig, Zeitsch. physikal. Chem. 1899, 31, 258; *ibid.* 1901, 37, 323; *ibid.* 38, 122; Price and Denning, *ibid.* 1903, 46, 89; Brossa, *ibid.* 1909, 66, 162; Spear, J. Amer. Chem. Soc. 1908, 30, 195; *see* also Kastel and Loevenhart, Amer. Chem. J. 1903, 29, 563; Liebermann, Ber. 1904, 37, 1519; Bredig, *ibid.* 798; Poppada, Gazz. chim. ital. 1907, 37, ii. 172).

Hydrogen peroxide is also decomposed by *catalases*, a class of organic ferments which are widely distributed in the animal and vegetable kingdoms (Senter, Proc. Roy. Soc. 1904, 74, 201; Wender, Chem. Zeit. 1904, 28, 30[illegible], [illegible], [illegible], Chem. Zentr. 1905, i. 941; Bach, Ber. 1904, 37, 3785; *ibid.* 1905, 38, 1878; Laer, Bull. Soc. chim. Belg. 1906, 19, 337; J. Inst. Brewing, 1906, 12, 313; Rywosch, Centr. Bakt. Par. 1907, i. 44, 295).

Hydrogen peroxide also acts as a deoxidising agent; thus silver oxide when brought in contact with it causes a mutual decomposition of the two compounds $Ag_2O+H_2O_2=H_2O+O_2+Ag_2$, an atom of oxygen is liberated from each compound, and a molecule of free oxygen is thus obtained. A similar reaction occurs when hydrogen peroxide and ozone are brought together, $H_2O_2+O_3=H_2O+2O_2$ (Mulder, Rec. trav. chim. 1903, 22, 388; Baeyer and Villiger, Ber. 1902, 34, 749; 2769; Inglis, Chem. Soc. Trans. 1903, 1013).

Hydrogen peroxide is reduced by manganese dioxide and peroxide of lead in presence of an acid, $H_2O_2+MnO_2=MnO+O_2+H_2O$.

Alkaline mercury salts are reduced to the metallic state by hydrogen peroxide (Kolk, Chem. Zeit. 1901, 25, 21). Direct sunlight accelerates the decomposition of hydrogen peroxide. The effect of hydrogen peroxide on a photographic plate is similar to that of light, and is probably due to the hydrogen peroxide vapour itself, and not to a radiation from it (Russell, J. Soc. Chem. Ind. 1899, 516; Otsuki, *ibid.* 1905, 575; Precht and Otsuki, *ibid.* 290; Dony-Hénault, *ibid.* 1904, 138; Graetz, Chem. Zentr. 1904, ii. 1561; Dony-Hénault, *ibid.* 1906, ii. 203; Bull. Soc. chim. Belg. 1908, 22, 224; Soeland, Ann. Physik. 1908, [iv.] 26, 899).

Hydrogen peroxide forms molecular compounds with certain inorganic and organic salts in which it appears to play the same part as water of crystallisation (Tanatar, Chem. Zeit. 1901, 25; Rep. 326; J. Russ. Phys. Chem. Soc. 1908, 40, 376; Staedel, *l.c.*; Jones and Carroll, Amer. Chem. J. 1902, 28, 284; Willstätter, Ber. 1903, 36, 1828; De Forcrand, Compt. rend. 1902, 134, 601).

An acidified solution of potassium dichromate in presence of hydrogen peroxide gives rise to an unstable combination of chromic acid and the dioxide; this, on mixing with ether, can be extracted from the aqueous solution, imparting to it a beautiful and characteristic blue colour.

A solution of guaiacum mixed with a small amount of blood gives a blue coloration on addition of hydrogen peroxide. This is a delicate test for the compound, and serves also as a test for blood.

Hydrogen peroxide gives a blue-green coloration with an alcoholic solution of guaiacol and sulphuric acid, and an intense yellow colour with a solution of quinine sulphate in concentrated sulphuric acid (Denigès, Pharm. J. 1909, July 31st).

In the presence of hydrogen peroxide, chlorates, bromates, iodates, phosphates, sulphates, hypochlorites, also salts of organic acids, give a yellow-green coloration with 1 p.c. guaiacol solution. On addition of hydrochloric or sulphuric acid the colour changes to red (Baudran, Compt. rend. 1905, 141, 891). Solutions of vanadic and titanic acids are turned brown or red by the peroxide, and with a mixture of potassium chlorate and aniline in the presence of acid a violet colour is formed after a short time (Bach, Compt. rend. 1894, 119, 1218); if dimethylaniline is used instead of aniline, a yellow colour is formed. By the latter reaction 1 part of peroxide in 5,000,000 can be detected.

When hydrogen peroxide is added to a solution of potassium iodide, even in presence of ferrous sulphate or copper sulphate, iodine is set free, which may be shown by the coloration of starch. Hydrogen peroxide is the only compound known which can liberate iodine in presence of ferrous sulphate (*cf.* Traube, Ber. 1884, 17, 1062), 1 part in 25,000,000 can thus be detected.

Tartaric acid added to hydrogen peroxide in presence of a ferrous salt gives on the addition of caustic alkali a violet coloration, due to the production of a ferric compound of deoxytartaric acid.

A very delicate reagent for hydrogen peroxide has been suggested by Charitschkoff (Chem. Zeit. 1910, 34, 50). It consists of the pinkish-red cobalt salts of the naphthenic acids obtained from the waste liquors from the refining of petroleum with alkali. A strip of filter paper is dipped into a petroleum solution of the cobalt salt, and, after drying, is moistened with the liquid to be tested. If the peroxide is present the colour changes immediately to olive-green. Ozone does not give this reaction.

An ammoniacal silver nitrate solution gives a characteristic grey opalescence or precipitate with hydrogen peroxide (von Sobbe, Chem. Zeit. 1911, 35, 898).

For other tests, *see* Denigès (Bull. Soc. chim. 1890, 797); Aloy (*ibid.* 1902, 27, 734); Precht and Otsuki (Zeitsch. physikal. Chem. 1905, 52, 236).

Technical applications.—Moistened lead sulphide in contact with hydrogen peroxide is quickly oxidised to lead sulphate. This fact has led to the employment of hydrogen peroxide as a *picture restorer.* The painting darkened by age or by exposure to air containing sulphuretted hydrogen, owing to the white lead employed as body colour being partially converted into lead sulphide, after careful treatment with an aqueous solution of the peroxide is found to be greatly improved in colour from the oxidation of the sulphide to the white sulphate.

Dilute solutions of hydrogen peroxide mixed occasionally with nitric acid, are also used as 'auricome,' 'golden hair water,' &c., for imparting a light colour to the hair (Schrötter, Ber. 1874, 7, 980; Lange, Dingl. poly. J. 1886, 259, 196).

It is also employed for removing the last traces of chlorine from vegetable fibres which have been bleached with the latter, and to remove the last traces of sulphur dioxide from bleached wool and silk.

Hydrogen peroxide may be used for bleaching in many cases where other agents, such as bleaching powder, sulphurous acid, chlorine, would be injurious. It is particularly valuable for bleaching ostrich feathers, bones, ivory, silk, wool, gelatin, straw, hair, parchment, wood, cotton, the teeth, &c.

The advantages of using hydrogen peroxide as a bleaching agent, particularly for wool, are claimed to be the following: a purer white can be obtained; the fibres are not tendered by it to the same extent as by the sulphur bleach; the wool, after bleaching, does not turn yellow, does not emit an unpleasant odour when in contact with perspiration, and purer tones and more even colours can be obtained on dyeing the bleached wool. It is also stated to be more convenient to use, more pleasant for the workpeople, and less corrosive on the machinery. With care, the process, moreover, need not be much more expensive than with the older bleaches, and it is now used very extensively and with good results, both in England and on the Continent (Wachtel, Farber-Zeit. 1900, 11, 268; Russell, Proc. Roy. Soc. 1899, 64, 409).

In the case of wool the scoured article is first soaked thoroughly in a dilute solution of sodium silicate (2 lbs. to 10 gallons). After saturation the wool is wrung out and placed in the peroxide bath, which is prepared by adding 3½ gallons of 10 volume peroxide to 6½ gallons of water in which ½ lb. of sodium silicate has been dissolved. The wool is kept in the bath for about 24 hours (or a shorter or longer interval depending on the quality of the wool and on the whiteness desired) at 80°F. Occasionally the wool is turned over, and the solution tested whether it is alkaline, which it must be for satisfactory results. It is then pressed through a wringing machine and dried at a temperature of 15°–17°C., and preferably in the sunlight. When quite dry the wool is well washed and redried (Fawsitt, J. Soc. Chem. Ind. 1902, 229; Luttringhaus, Färber-Zeit. 1901, 12, 328; Dommergne, Rev. Chim. Ind. 1896, 7, 73).

With slight modifications this process is also applicable to cotton, straw and silk, but for the two last, the peroxide solution is made up of 1 part 10 volumes peroxide to 2 of water, and for every 10 volumes of peroxide, 4 ozs. of sodium silicate are employed (Fawsitt, *l.c.*; Koechlin, J. Soc. Chem. Ind. 1899, 1119). In the case of silk the bath may be made strongly alkaline with caustic soda from the beginning of the process.

Bone and ivory are first cleansed by treatment with light petroleum, ammonia or other solvent; they are then immersed in a bath containing 1 of 10 volumes peroxide to 2 of water made slightly alkaline with ammonia. Feathers are bleached similarly, but are washed after bleaching with a dilute solution of sulphuric acid.

On a small scale lace can be bleached conveniently in the following way: The material, after being moistened with water, is immersed in a solution of potassium permanganate for a few minutes. It is then rinsed and treated for about 10 minutes with a very dilute solution of hydrogen peroxide, after which it is treated with acid to remove the manganous oxide formed in the previous operation (Thomas, J. Soc. Chem. Ind. 1900, 734).

For bleaching delicate materials the hydrogen peroxide should not be too strong; a solution of 1 in 10 is strong enough, and a bleaching vat of this solution may be used for a long time if the strength be kept up by fresh additions of hydrogen peroxide. In bleaching dead hair, it is first digested for 12 hours in a solution of 3 parts of ammonium carbonate in 100 of water at a temperature of 30°C., rinsed, then washed with soap and treated with ammonium carbonate until all fatty matter is removed. Thus prepared it is treated in a bath of hydrogen peroxide and water as in the first case.

Hydrogen peroxide has been used for tanning leather, also to disinfect hides that have been long stored, and to preserve extracts of tanning materials (Göhring, J. Soc. Chem. Ind. 1890, 84). It has also been recommended for use in photographic processes (Smith, J. 1873, 1131; Gros, D. R. PP. 147131; 153769; 158368; Otsuki, *l.c.*; Lüppo Cramer, Chem. Zeit. 1902, 26, Rep. 292, 336; Ebert, *ibid.* 27, Rep. 152).

Medicinal and surgical applications.—As an antiseptic and disinfectant it has the advantage of (1) being odourless; (2) yielding oxygen without leaving any residuum but pure water; (3) absence of injurious influence on the organism.

The antiseptic properties of hydrogen peroxide solution were first brought into notice by Richardson in 1860. They were also studied by Kingzett, and subsequently by Paul Bert and Regnard (Compt. rend. 1882, 94, 1383).

It is used in the treatment of syphilitic and scrofulous sores, alveolar abscesses, and purulent discharges. It is also of great value in cases of purulent discharge from the conjunctiva, and it is particularly efficient for destroying diphtheritic membranes.

Its behaviour is that of a powerful oxidising agent, but on healthy skin its action is slow. In contact with fistulous wounds or pus it is rapidly decomposed with effervescence, which continues till the wound is cleansed or the diseased secretion is destroyed (Kingzett, J. Soc. Chem. Ind. 1890, 3; Paneth, Chem. Zentr. 1890, 174; Schmidt, *ibid.* 1906, ii. 145; Jaubert, *ibid.* 1905, ii. 99).

Hydrogen peroxide may be used to bleach discoloured teeth. In cases where the teeth are covered with coloured matter (*Lichen dentalis*, &c.) peroxide of hydrogen in conjunction with finely levigated pumice-stone may be employed in place of water. A suitable liquid for cleansing the teeth and mouth is prepared by mixing 1 part of 3 p.c. peroxide of hydrogen with 9 parts of water (Chem. News, 45, 71; and Ch. Trade J. April 14, 1888).

It has been proposed to use mixtures of hydrogen peroxide containing starch, cooked or in viscid solution, with anhydrous calcium sulphate as dentrifices, the starch preventing loss of oxygen from the oxide and the latter preserving the starch from putrefaction (Queissier, Fr. Pat. 381024, 1907; J. Soc. Chem. Ind. 1908, 226).

Hydrogen peroxide has the power of freeing water from living organisms, a property which has been utilised in brewing. It also destroys the acid and mould ferments in the wort, and has been used in sterilising casks and filter pulp. In stronger doses it destroys the alcoholic ferment and stops fermentation (G. Reisenbichler, Chem. News, 56, 219; Miquel, Monit. Scient. 1884, [3] 14, 170; Chodat and Bach, Ber. 1902, 35, 1275; Loew, *ibid.* 2487; Bonjean, Compt. rend. 1905, 140, 50; Laer, J. Inst. Brewing, 1909, 15, 553).

Altenhöfer has recommended hydrogen peroxide as a disinfectant for drinking water (Zentr. Bakteriol and Parasitenkde, 1890, 129; Küster, Chem. Zentr. 1880, i. 411; 1891, ii. 272; 1895, i. 948; but see also Gourmont, Nagier, and Rochaix, Compt. rend. 1910, 150, 1453).

Hydrogen peroxide is one of the chief constituents of 'Sanitas,' which is a solution of the products of oxidation of turpentine oil in the presence of water and air (Kingzett).

It has been tried with success in the preservation of beer; after a month the taste and aroma of the beer remained good (Weingartner, Bied. Zentr. 1884, 428).

Hydrogen peroxide has been suggested as a useful and harmless preservative of milk (Jablin and Gounet, Ann. Chim. anal. 1901, 6, 129; J. Soc. Chem. Ind. 1902, 420; *ibid.* 1905, 1184; Fr. Pat. 355547; Amberg, J. Biol. Chem. New York, 1906, i. 219).

To test milk for hydrogen peroxide, 10 drops of a 2 p.c. alcoholic solution of benzidine and a few drops of acetic acid are added to 10 c.c. of the milk. If hydrogen peroxide is present a blue coloration appears. The peroxide can be detected in this way in other liquids if a little milk serum is added (Wilkinson and Peters, Zeitsch. Nahr. Genussm. 1908, 16, 172, 515, 589; for other tests, *see* Feder, *ibid.* 15, 234; Arnold and Mentzel, *ibid.* 1903, 6, 305).

Hydrogen peroxide is used in the laboratory in the valuation of bleaching-powder, the principle depending upon the fact that hypochlorites, when mixed with hydrogen peroxide, instantly evolve all their oxygen, at the same time liberating the oxygen of the peroxide (J. Soc. Chem. Ind. 1887, 391). It is also employed in estimating the amount of active oxygen in potassium permanganate and in manganese dioxide (Schlossberg, Zeitsch. anal. Chem. 1902, 41, 735; Carnot, Compt. rend. 1893, 116, 1295). The amount of sulphur in sulphides is also determined by first oxidising to sulphate and then proceeding as usual (G. Lunge, Ber. 18, 1872; *see* also Baumann, Zeitsch. angew. Chem. 1890, 72; Talbot and Moody, J. Soc. Chem. Ind. 1893, 780).

Hydrogen peroxide has been employed in the separation of a number of metals from one another (Rose, Ber. 1894, 27, 2227; Lesinsky, *ibid.* 1893, 26, 1496, 2331, 2908; Jannasch and Röttgen, Zeitsch. anorg. Chem. 1895, 8, 202; Friedheim and Bruhl, Zeitsch. anal. Chem. 1899, 38, 681). Also for the separation of the halogens (Jannasch and Zimmermann, Ber. 1906, 39, 196, 3655). and for separating vanadium from ores and slags (Fr. Pat. 357397; J. Soc. Chem. Ind. 1906, 72).

Hydrogen peroxide has also been used as a solvent for Indian gum (Bull. Soc. Ind. Mulhouse, 1894, 36), but its use in the estimation of the quantity of flour in a mixture of the latter with bran, is considered to be untrustworthy by Bremer (Zeitsch. Nahr. Genussm. 1906, 11, 569).

Hydrogen peroxide has been employed with success in determining the amount of sulphur in coal gas. The solution used for this purpose consists of the commercial product diluted to a 1 p.c. solution. This solution is run into the Referees' 'apparatus,' through which the coal gas passes at a measurable rate, and the sulphurous acid gas in it is oxidised to sulphuric acid $SO_2+H_2O_2=SO_4H_2$. The amount of sulphur is then determined by titration or precipitation (J. Soc. Chem. Ind. 1887, 285).

Higher oxides of hydrogen.—The oxides H_2O_4 and H_2O_5 have been described (Bach, Ber. 1900, 33, 1506, 3111; *ibid.* 1902, 35, 158; Berthelot, Compt. rend. 1900, 131, 637), but it is doubtful whether they really exist (Armstrong, Chem. Soc. Proc. 1900, 134; Ramsay, Chem. Soc. Trans. 1901, 1324; *see* also Baeyer and Villiger, 1900, 33, 2488; Clover, Amer. Chem. J. 1903, 24, 463; Brühl, Chem. Zentr. 1896, i. 86; Nagel, Pharm. Zeit. 1898, 43, 556). Kastner (J. 1820, 472) described a *suboxide*, but its existence has not been confirmed.

HYDROGEN SULPHIDES *v.* SULPHUR.

HYDROHÆMATITE *v.* TURGITE.

HYDROLITES *v.* AGATE.

HYDROLYSIS. The term hydrolysis (or hydrolytic dissociation) is given to a number of different chemical reactions, all of which consist in the addition of water to a complex, and the subsequent resolution of the product into simpler substances.

Some of the best-known types of hydrolysis are those of metallic salts, esters, acid chlorides, amides, &c., or generally acyl derivatives, complex carbohydrates, and glucosides, and finally, polypeptides and proteins.

I. **Hydrolysis of salts.** The hydrolysis of a salt by water may be represented by means of an equation of the type:

$$KCN + H{\cdot}OH \leftrightarrows HCN + KOH$$

The reaction is a balanced one, and may be regarded as due to the incomplete neutralisation of the acid and base from which the salt is derived; in terms of the ionic theory the acid in question (HCN) does not yield sufficient hydrions to combine with the hydroxyl ions of an equivalent quantity of the strong base (KOH). When equivalent quantities of a strong acid and a strong base are brought together in aqueous solution complete neutralisation takes place, and a normal salt with a neutral reaction towards common indicators is formed. (Basis of methods of acidimetry and alkalimetry.) In the cases of such salts appreciable hydrolysis would not be expected even in dilute solution. The following are the common types of salts which are hydrolysed by water: (1) salts derived from feeble acids and strong bases; (2) salts from strong acids and feeble bases; (3) salts from feeble acids and feeble bases. As examples of the first type we have potassium cyanide and sodium phosphate,

$$KCN + H{\cdot}OH \rightleftarrows HCN + KOH$$

$$Na_3PO_4 + H{\cdot}OH \rightleftarrows Na_2HPO_4 + NaOH$$

and even

$$Na_2HPO_4 + H{\cdot}OH \rightleftarrows NaH_2PO_4 + NaOH$$

Solutions of such salts invariably have an alkaline reaction towards common indicators, *e.g.* litmus, phenolphthalein. The water may be regarded as a feeble acid, which, like any other feeble acid, liberates a certain amount of acid from the salt with which it is brought into contact. In many cases acid salts are first formed, *e.g.* sodium phosphate, sodium carbonate, but free acid and free base may be liberated. The alkaline reaction of the solution can be accounted for by the fact that the feeble acid, or the acid salt formed, is ionised to a slight extent only, whereas with moderately dilute solutions the strong base is almost completely ionised, and thus there is a great excess of hydroxyl ions over hydrions. As examples of the second type we have ferric chloride and cupric sulphate, which are derived respectively from the feeble bases, ferric hydroxide and cupric hydroxide. The aqueous solutions of such salts invariably give an acid reaction. The hydrolysis may be represented by means of the equations:

$$FeCl_3 + H{\cdot}OH \leftrightarrows FeCl_2{\cdot}OH + HCl$$

or even $FeCl_3 + 3H{\cdot}OH \leftrightarrows Fe(OH)_3 + 3HCl$

and $CuSO_4 + 2H{\cdot}OH \leftrightarrows Cu(OH)_2 + H_2SO_4$

With moderately concentrated solutions basic salts, *e.g.* $FeCl_2{\cdot}OH$ are almost certainly formed, and it is only in very dilute solution that the hydrolysis will proceed to the formation of the metallic hydroxide, and even when this is formed it is not precipitated, but remains in solution in the form of a colloid. A group of salts which belongs to this type is that of the salts derived from feeble organic bases such as aniline, and from the strong mineral acids, *e.g.*

$$\underset{\text{Aniline hydrochloride.}}{C_6H_5{\cdot}NH_3Cl} + H{\cdot}OH \rightleftarrows \underset{\text{Aniline hydroxide.}}{C_6H_5{\cdot}NH_3{\cdot}OH} + HCl$$

$$\rightleftarrows C_6H_5NH_2 + H_2O + HCl$$

As examples of the third type we have ferric phosphate, aluminium carbonate and sulphide, and aniline acetate. The hydrolysis in the first case is readily shown by washing finely divided ferric phosphate with distilled water, when it is found that the filtrate is always distinctly acid, owing to the free phosphoric acid which has been washed away by the water, and if the operation is continued nearly pure ferric hydroxide remains on the filter. In the case of the two aluminium salts, they are so readily hydrolysed that when brought into contact with water they yield the corresponding metallic hydroxide, and the free acids, carbonic acid and hydrogen sulphide, which escape and thus destroy the equilibrium.

In the case of salt formation we may regard the water as capable of acting as either a feeble base or a feeble acid. When in contact with equivalents of a strong acid and a feeble base the water competes with the base for the acid, and hence neutralisation is not complete, or, in other words, hydrolysis of the salt occurs and the feebler the base the greater the degree of hydrolysis. The mechanism of salt hydrolysis according to the ionic theory is as follows: In aqueous solution the given salt, *e.g.* potassium cyanide is ionised in the ordinary manner into $\overset{+}{K}$ and $\overset{-}{CN}$ ions, but water itself is ionised to a certain extent, $H_2O \rightleftarrows \overset{+}{H} + \overset{-}{OH}$, and as hydrogen cyanide is a very feeble acid, and therefore ionised to only a very slight extent in aqueous solution, there is a tendency for the $\overset{+}{H}$ ions of the water to combine with the $\overset{-}{CN}$ ions from the cyanide, yielding undissociated HCN, the result is that the equilibrium $H_2O \rightleftarrows \overset{+}{H} + \overset{-}{OH}$ is destroyed and more molecules of water are ionised, but this results in further combination between $\overset{+}{H}$ and $\overset{-}{CN}$ ions, and by this means an excess of $\overset{-}{OH}$ over $\overset{+}{H}$ ions is produced, and thus the alkaline reaction. The changes continue until ultimately an equilibrium is established between the KCN, $\overset{-}{\mathrm{CN}}$, $\overset{+}{\mathrm{K}}$, $\overset{+}{\mathrm{H}}$, $\overset{-}{\mathrm{OH}}$, HCN, and H_2O present. The degree of hydrolysis, *i.e.* the fraction of the salt hydrolysed, cannot be determined by direct titration of the free acid or free base present in the solution; the addition of standard acid to the solution of potassium cyanide would immediately destroy the equilibrium which previously existed, and more salt would be hydrolysed in order to restore the equilibrium, and the point of neutrality would not be reached until acid sufficient to decompose the salt completely had been added. The methods commonly adopted for determining the degree of hydrolysis are (*cf.* Farmer, B. A. Report, 1901, 240): 1. Determination of the concentration of the free acid or free alkali present in the solution of the salt by its catalytic effect on the hydrolysis of an aqueous solution of ethyl acetate or on the inversion of a solution of cane sugar, and then determining the amount of pure acid or alkali required to produce the same effect (for acid, *cf.* Walker, Zeitsch. physikal. Chem. 1889, 4, 319; for alkali, *cf.* Shields, *ibid.* 1893, 12, 167; also Bruner, *ibid.* 1900, 32, 133; Ley, *ibid.* 1899, 30, 216; Walker and Aston, Chem. Soc. Trans. 1895, 67, 576). 2. Determination of the electrical conductivity of the solution (Walker, Zeitsch. physikal. Chem. 1889, 4, 333; Bredig, *ibid.* 1894, 13, 313; Lundy, J. Chim. Phys. 1907, 5, 574; Denham, Chem. Soc. Trans. 1908, 93, 41). The molecular conductivity of a hydrolysed salt of the type aniline hydrochloride is made up of two quantities: (*a*) conductivity due to the non-hydrolysed salt; (*b*) conductivity due to the free acid formed on hydrolysis—since the free base (aniline) is not an electrolyte. $M = (1-x)u_1 + xu_{HCl}$, where M = molecular conductivity, x=degree of hydrolysis, u_1=molecular conductivity of non-hydrolysed salt. The various quantities in the equation with the exception of x can be determined and then x calculated. 3. By determining the partition coefficient (Farmer, Chem. Soc. Trans. 1901, 79, 863). In the case of aniline hydrochloride the hydrolysis of the salt leads to the formation of free aniline and hydrochloric acid, and the concentration of the free base is determined by shaking the aqueous solution at a given temperature with a known volume of benzene, and finding the concentration of the aniline in the benzene layer. Since C_B/C_{Aq} is always constant (C_B=concentration of aniline in benzene and C_{Aq}=concentration of aniline in water) for a given temperature the concentration of free aniline in the aqueous layer can be calculated directly, and thus the degree of hydrolysis determined. The assumption is made that the salt present does not affect the partition coefficient to an appreciable extent. 4. By the change in colour produced by a solution of the hydrochloride of an organic base on a solution of methyl orange of known concentration, and a comparison of this change with that produced by the addition of known quantities of hydrochloric acid (Veley, Chem. Soc. Trans. 1908, 93, 652, 1114, 2122; 1909, 95, 758; Trans. Far. Soc. 1908, 4, 19).

Most of the methods give only rough approximations (cp. Beveridge, Proc. Roy. Soc. Edin. 1909, 29, 648). A few of the results obtained are as follows:—

Salt	Temp. °	P.c. of salt hydrolysed in 0·1 N solution	Method
Glycine hydrochloride	25	19·00	Hydrolysis of ester
Acetoxime ,,	25	36·00	,, ,,
Urea ,,	25	90·00	,, ,,
Urea ,,	60	81·00	Inversion of sugar
Sodium cyanide .	25	1·10	Saponification of ester
,, acetate .	25	0·008	,, ,,
,, carbonate .	25	3·17	,, ,,
,, phenate .	25	3·05	,, ,,
Aniline hydrochloride	60	2·60	Inversion of sugar
,, ,,	25	1·50	Conductivity
Zinc chloride . .		0·10	Inversion of sugar
Aluminium chloride	100	6·10	,, ,,
,, ,, .	100	0·50	Conductivity
Ferric chloride . .	25	10·00	Inversion of sugar
Lead ,, . .	40	0·50	Conductivity
	25		

The whole question becomes more complicated when the acid or base formed by hydrolysis is unstable and is transferred into an isomeride (pseudo-acid or pseudo-base).

The influence of concentration on hydrolysis is given by Guldberg and Waage's law of mass action. According to this $\frac{C_S}{C_A \times C_B}$=constant, where C_S represents the concentration (molar) of the non-hydrolysed salt, C_A that of the acid formed by hydrolysis, and C_B that of the base. If originally 1 gram. mol. of salt was dissolved in v litres of solution and x gram mols. were hydrolysed, then

$$\frac{1-x}{v} \Big/ \frac{x}{v}\cdot\frac{x}{v} = \text{constant, or } \frac{v(1-x)}{x^2} = \text{constant.}$$

It is obvious that as v increases, *i.e.* as the concentration is diminished, x, *i.e.* the degree of hydrolysis, must increase in order to keep the whole expression constant.

The relationships are not quite the same in the case of a salt derived from a feeble base and a feeble acid, *e.g.* aniline acetate,

$$C_6H_5{\cdot}NH_3{\cdot}O{\cdot}CO{\cdot}CH_3 + H_2O \rightleftarrows C_6H_5{\cdot}NH_3{\cdot}OH + CH_3{\cdot}CO{\cdot}OH$$

If the reaction is represented as taking place between the ions of the salt and the water, and the salt is practically completely ionised, and the base and acid not appreciably, then $C_{Cat}{\cdot}C_{An}/C_A{\cdot}C_B$=constant, where C_{Cat}=concentration of the cation and C_{An}=concentration of the anion. But $C_{Cat}=C_{An}=C_{Salt}$.

$$\therefore C^2_{Salt}/C_A{\cdot}C_B=\text{constant, or} \left(\frac{s}{v}\right)^2 \Big/ \frac{a}{v}\cdot\frac{b}{v}=\text{constant}$$

where s, a, b are the gram mols. respectively of salt, acid, and base in v litres of solution. But this expression is independent of v, and hence dilution does not affect the degree of hydrolysis.

Another factor which affects the degree of hydrolysis is the addition to the solution of one of the products of hydrolysis, *e.g.* free acid or free base. Thus the hydrolysis of aniline hydrochloride in aqueous solution can be stopped

Ber. 1900, 33, 1506, 3111; *ibid.* 1902, 35, 158; Berthelot, Compt. rend. 1900, 131, 637), but it is doubtful whether they really exist (Armstrong, Chem. Soc. Proc. 1900, 134; Ramsay, Chem. Soc. Trans. 1901, 1324; *see* also Baeyer and Villiger, 1900, 33, 2488; Clover, Amer. Chem. J. 1903, 24, 463; Brühl, Chem. Zentr. 1896, i. 86; Nagel, Pharm. Zeit. 1898, 43, 556). Kastner (J. 1820, 472) described a *suboxide*, but its existence has not been confirmed.

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I. **Hydrolysis of salts.** The hydrolysis of a salt by water may be represented by means of an equation of the type:

$$KCN + H\cdot OH \leftrightarrows HCN + KOH$$

The reaction is a balanced one, and may be regarded as due to the incomplete neutralisation of the acid and base from which the salt is derived; in terms of the ionic theory the acid in question (HCN) does not yield sufficient hydrions to combine with the hydroxyl ions of an equivalent quantity of the strong base (KOH). When equivalent quantities of a strong acid and a strong base are brought together in aqueous solution complete neutralisation takes place, and a normal salt with a neutral reaction towards common indicators is formed. (Basis of methods of acidimetry and alkalimetry.) In the cases of such salts appreciable hydrolysis would not be expected even in dilute solution. The following are the common types of salts which are hydrolysed by water: (1) salts derived from feeble acids and strong bases; (2) salts from strong acids and feeble bases; (3) salts from feeble acids and feeble bases. As examples of the first type we have potassium cyanide and sodium phosphate,

$$KCN + H\cdot OH \rightleftarrows HCN + KOH$$

$$Na_3PO_4 + H\cdot OH \rightleftarrows Na_2HPO_4 + NaOH$$

and even

$$Na_2HPO_4 + H\cdot OH \rightleftarrows NaH_2PO_4 + NaOH$$

Solutions of such salts invariably have an alkaline reaction towards common indicators, *e.g.* litmus, phenolphthalein. The water may be regarded as a feeble acid, which, like any other feeble acid, liberates a certain amount of acid from the salt with which it is brought into contact. In many cases acid salts are first formed, *e.g.* sodium phosphate, sodium carbonate, but free acid and free base may be liberated. The alkaline reaction of the solution can be accounted for by the fact that the feeble acid, or the acid salt formed, is ionised to a slight extent only, whereas with moderately dilute solutions the strong base is almost completely ionised, and thus there is a great excess of hydroxyl ions over hydrions. As examples of the second type we have ferric chloride and cupric sulphate, which are derived respectively from the feeble bases, ferric hydroxide and cupric hydroxide. The aqueous solutions of such salts invariably give an acid reaction. The hydrolysis may be represented by means of the equations:

$$FeCl_3 + H\cdot OH \leftrightarrows FeCl_2\cdot OH + HCl$$

or even $FeCl_3 + 3H\cdot OH \leftrightarrows Fe(OH)_3 + 3HCl$

and $CuSO_4 + 2H\cdot OH \leftrightarrows Cu(OH)_2 + H_2SO_4$

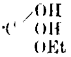
With moderately concentrated solutions basic salts, *e.g.* $FeCl_2\cdot OH$ are almost certainly formed, and it is only in very dilute solution that the hydrolysis will proceed to the formation of the metallic hydroxide, and even when this is formed it is not precipitated, but remains in solution in the form of a colloid. A group of salts which belongs to this type is that of the salts derived from feeble organic bases such as aniline, and from the strong mineral acids, *e.g.*

$$\underset{\text{Aniline hydrochloride.}}{C_6H_5\cdot NH_3Cl} + H\cdot OH \rightleftarrows \underset{\text{Aniline hydroxide.}}{C_6H_5\cdot NH_3\cdot OH} + HCl$$

$$\rightleftarrows C_6H_5NH_2 + H_2O + HCl$$

As examples of the third type we have ferric phosphate, aluminium carbonate and sulphide, and aniline acetate. The hydrolysis in the first case is readily shown by washing finely divided ferric phosphate with distilled water, when it is found that the filtrate is always distinctly acid, owing to the free phosphoric acid which has been washed away by the water, and if the operation is continued nearly pure ferric hydroxide remains on the filter. In the case of the two aluminium salts, they are so readily hydrolysed that when brought into contact with water they yield the corresponding metallic hydroxide, and the free acids, carbonic acid and hydrogen sulphide, which escape and thus destroy the equilibrium.

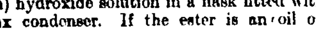
In the case of salt formation we may regard the water as capable of acting as either a feeble base or a feeble acid. When in contact with equivalents of a strong acid and a feeble base the water competes with the base for the acid, and hence neutralisation is not complete, or, in other words, hydrolysis of the salt occurs and the feebler the base the greater the degree of hydrolysis. The mechanism of salt hydrolysis according to the ionic theory is as follows: In aqueous solution the given salt, *e.g.* potassium cyanide is ionised in the ordinary manner into $\overset{+}{K}$ and $\overset{-}{CN}$ ions, but water itself is ionised to a certain extent, $H_2O \rightleftarrows \overset{+}{H} + \overset{-}{OH}$, and as hydrogen cyanide is a very feeble acid, and therefore ionised to only a very slight extent in aqueous solution, there is a tendency for the $\overset{+}{H}$ ions of the water to combine with the $\overset{-}{CN}$ ions from the cyanide, yielding undissociated HCN, the result is that the equilibrium $H_2O \rightleftarrows \overset{+}{H} + \overset{-}{OH}$ is destroyed and more molecules of water are ionised, but this results in further combination between $\overset{+}{H}$ and $\overset{-}{CN}$ ions, and by this means an excess of $\overset{-}{OH}$ over $\overset{+}{H}$ ions is produced, and thus the of the ethyl esters of propionic, acrylic, butyric, crotonic, $\beta\alpha$-phenylpropionic, and cinnamic acids with dilute hydrochloric acid at 20°. Williams and Sudborough (Chem. Soc. Trans. 1912, 101, 412) show that the rate of hydrolysis of the ethyl ester of an $\alpha\beta$ unsaturated compared with the rate for the corresponding saturated acid is about 1 : 30. The difference is, however, not nearly so marked when an alkali (barium hydroxide) is used as hydrolysing agent.

The majority of chemists are of opinion that the process of hydrolysis consists first of all in the formation of an additive compound between the ester and the water, *e.g.*  $R\cdot C\begin{smallmatrix}\diagup OH\\ -OH\\ \diagdown OEt\end{smallmatrix}$ (*cp.* Esterification), and the subsequent breaking up of this into acid and alcohol. The manner in which the complex dissociates, *e.g.* into water and ester, or into alcohol and acid, will depend largely on the relative amounts of water and alcohol present. A view put forward by Stieglitz, and supported by many chemists (*cp.* Acree and Johnson, Amer. Chem. J. 1907, 38, 335), is that the ester, being a feeble base, combines with the strong mineral acid used as catalyst, forming a salt, *e.g.* $R\cdot CO_2Et,HCl$, only small amounts of such salts would be formed, as the base is an extremely feeble one. The salt would be ionised in the usual manner into $\overset{-}{Cl}$ ions and complex cations $R\cdot C\overset{+}{O_2}Et,H$. It is these complex cations which then react with the water and undergo hydrolysis

$$R\cdot CO_2\overset{+}{E}t,H+H_2O=R\cdot CO_2H+EtOH+\overset{+}{H}$$

and the assumption has to be made that the hydrolysis of the complex cations proceeds more rapidly than the hydrolysis of the ester molecules. The view that it is the complex cation and not the unionised salt (ester hydrochloride) which reacts with the water is supported by the fact that the rate of hydrolysis is directly proportional to the concentration of the mineral acid, *i.e.* to the concentration of the hydrion and not to the square of the concentration of the hydrion.

The hydrolysis of an ester by means of an alkali hydroxide can be represented by an equation of the type :



$$R\cdot C\begin{smallmatrix}\diagup O\\ \diagdown OEt\end{smallmatrix}+KOH=R\cdot C\begin{smallmatrix}\diagup O\\ \diagdown OK\end{smallmatrix}+EtOH$$

The reaction is non-reversible, as the alkali salt cannot react directly with the alcohol, and as both ester and alkali are used up as the hydrolysis proceeds the reaction should be bimolecular. Hydrolysis by alkalis proceeds more rapidly than that by mineral acids (*cp.* Van Dijken, Rec. trav. chim. 1895, 14, 106), and is the common method used in the laboratory. The ester is boiled for some time with an excess of sodium (or potassium) hydroxide solution in a flask fitted with a reflux condenser. If the ester is an oil only sparingly soluble in water, the completion of the reaction is denoted by the disappearance of the oily layer, unless the alcohol formed is also insoluble in water. If, however, the ester itself is soluble in water, but has a characteristic odour, the disappearance of the odour indicates complete hydrolysis. In order to separate the acid and alcohol formed, the mixture is (*a*) boiled, when the alcohol passes over together with water, provided the alcohol is a comparatively simple monohydric one; (*b*) extracted with ether if the alcohol is complex and is not readily volatile. To obtain the acid the alkaline solute left after treatment (*a*) or (*b*) is acidified with hydrochloric acid, when the organic acid is directly precipitated if it is sparingly soluble in water, or can be extracted with ether if soluble in water.

An alcoholic solution of potassium hydroxide is sometimes used for hydrolysing purposes, especially when the ester is practically insoluble in water.

The decomposition of esters by alkaline hydroxide solutions is the basis for the usual methods for the manufacture of hard and soft soaps (*see* SOAP; SAPONIFICATION), and hence a common name for the process is '*saponification*.' The common fats are glyceryl esters of monobasic acids of high molecular weight, more especially of palmitic, stearic, and oleic acids, and on saponification yield the trihydric alcohol glycerol and the sodium or potassium salts of the acids, *e.g.*

$$C_3H_5(O\cdot CO\cdot C_{17}H_{35})_3+3NaOH$$
$$=C_3H_5(OH)_3+3C_{17}H_{35}\cdot COONa$$

Anderson and Brown (J. Phys. Chem. 1916, 20, 195) have studied the velocity of saponification of various fats in different media; they find that the velocity is practically independent of the molecular weight of the fat, but varies considerably with the solvent and of the three used, namely, methyl, ethyl, and amyl alcohols, is greatest in amyl alcohol.

The saponification of fat occurs in stages and if insufficient alkali is used, the product is a mixture of unaltered fat with mono- and diglycerides and free fatty acid (*cf.* Fortine Chem. Zeit. 1912, 36, 1117; Marcusson, Zeitsch. angew. Chem. 1913, 26, 173).

Reicher (Annalen, 1885, 228, 257) was one of the first to determine the velocity of saponification under varying conditions. When the alkali and ester are not used in equivalent quantities the differential equation is of the type

$$dx/dt=K(a-x)(b-x)$$

where a and b are the original concentrations, and $a-x$ and $b-x$ the concentrations at the time t. When integrated this gives an equation

$$K=\frac{1}{t(a-b)}\log_e\frac{b(a-x)}{a(b-x)}$$

for calculating K. The concentration of the alkali at any given time is determined by titration with standard acid and the concentration of the ester calculated from that of the alkali, as with an ester of the type of ethyl acetate, the disappearance of each gram molecule of alkali entails the disappearance of a gram molecule of ester (*cf.* Warder, Amer. Chem. J. 1882, 3, 340; Ber. 1881, 14, 1311). The velocity constant K can be calculated by means of the equation

$$K=\frac{1}{C_{\infty}t}\log_e\frac{C_t(C-C_{\infty})}{C(C_t-C_{\infty})}$$

where C, C_t, and C_{∞} denote the concentration of the alkali just after mixing, the concentration after time t and the concentration after complete hydrolysis (24–48 hours).

Reicher's experiments were carried out at 9·4°, and show that the velocity is practically the same whether sodium, potassium, or calcium hydroxide is used as saponifying agent. With strontium or barium hydroxide the velocity constants are somewhat smaller and with a feeble alkali, such as ammonium hydroxide, the value for K is much less, *e.g.*

$$K_{\mathrm{NaOH}} : K_{\mathrm{NH_4OH}} = 200 : 1.$$

The results obtained by using different esters show that the alkyl group R′ in the ester $\mathrm{R{\cdot}C}{<}^{\mathrm{O}}_{\mathrm{OR'}}$ influences the rate of hydrolysis to a greater extent than it does when mineral acids are used for hydrolysing; thus the values for K using sodium hydroxide at 9·4° are: methyl acetate 3·49, ethyl acetate 2·31, propyl acetate 1·92, *iso*butyl acetate 1·62, and *iso*amyl acetate 1·64. The influence of the acyl group R·CO is also marked, as shown by the following values for K at 14·4°, using sodium hydroxide and ethyl esters: acetate 3·2, propionate 2·8, butyrate 1·7, *iso*butyrate 1·73, *iso*valerate 0·62, and benzoate 0·83. Later experiments by Sudborough and Feilmann (Chem. Soc. Proc. 1897, 13, 243) prove that the introduction of methyl groups into the ethyl acetate molecule retards hydrolysis by means of alcoholic potassium hydroxide, whereas the introduction of chlorine atoms facilitates the decomposition. The investigations of Gyr (Ber. 1908, 41, 4308) show that two or three phenyl groups in the ethyl acetate molecule also retard hydrolysis, whereas the ethyl ester of phenylacetic acid is hydrolysed more readily than ethyl acetate itself. The results obtained by Hjelt (Ber. 1896, 29, 1864) with substituted derivatives of ethyl malonate also show that the introduction of an alkyl group into the ethyl malonate molecule retards hydrolysis, and that when two such groups are present the effect is still more noticeable. The influence of the strength of the acid from which the ester is derived also appears to be a determining factor. The investigations of Kellas (Zeitsch. physikal. Chem. 1897, 24, 243) on the hydrolysis of ethyl esters of substituted benzoic acids show that the esters of many substituted benzoic acids are hydrolysed by alcoholic potash more readily than ethyl benzoate itself. This appears to be true of all esters derived from acids much stronger than benzoic acid, *e.g.* the bromo-, chloro-, and nitro-benzoic acids, but does not hold good when the esters are derived from acids with small dissociation constants, *e.g.* the toluic acids. Kellas's results also show that when the rates of hydrolysis of a group of three isomeric esters are compared the ortho-compounds are invariably hydrolysed more slowly than the isomeric, meta-, and para- compounds, even when the ortho- acid is a much stronger acid than the isomers.

Findlay and Turner (Chem. Soc. Trans. 1905, 87, 747) and Findlay and Hickmans (*ibid.* 1909, 95, 1004) show that an *a*-hydroxyl group increases the readiness with which the ester is hydrolysed by alkalis. The ratio K ethyl glycollate : K ethyl acetate = 11·5; and K ethyl lactate : K ethyl propionate = 11·9, and K methyl mandelate : K methyl phenylacetate = 5·7. The introduction of a phenyl group in the *a*-position does not necessarily increase the rate of hydrolysis. The ratio K ethyl phenylacetate : K ethyl acetate = 1·9, but K ethyl mandelate : K ethyl glycollate = 0·88. It is shown that there is no direct proportionality between the affinity constant of the acid and the saponification constant of its ester, although in any given series of compounds the two constants follow the same order. Palomaa (Chem. Soc. Abstr. 1914, i. 136) shows that with esters which contain an oxygen atom in the chain (whether as OH, OR, CO, or O) the velocity of hydrolysis by mineral acids is reduced to a minimum when the oxygen atom is in the *β*-position with respect to the ester group. On the other hand, a cyano group always has a retarding effect on the hydrolysis of an ester by dilute hydrochloric acid, and the effect is more pronounced in the *a*- than in the *β*-position (Amer. J. Sci. 1914, [iv.] 37, 514). Drushel and Dean (*ibid.* 1912, [iv.] 34, 293) show that in the case of acetic acid the rate of hydrolysis is increased by the introduction of the hydroxy group, but retarded by an alkyloxy group. The introduction of hydroxy groups into the butyric acid, on the other hand, had a retarding effect (Dean, *ibid.* 1914, [iv.] 37, 331). For hydrolysis of halogenated esters, *see* Drushel, *ibid.* 1912, [iv.] 34, 69; for hydroxy and alkyloxy derivatives of propionic acid, *ibid.* 1913, [iv.] 35, 486. When alkali is used for hydrolysing the esters of hydroxy acids (*ibid.* 905) the esters derived from strong acids are more readily saponified than those from weak. The results obtained by different authorities point to the general conclusion that two factors at least determine the rate of hydrolysis of ethyl esters by alkalis or acids. (*a*) The complexity of the acyl group, especially as regards the presence of substituents in close proximity to the carbonyl group, *e.g.* in the *a*-position in aliphatic, the ortho- position in aromatic, and probably the cis- position in unsaturated esters. (*b*) The strength of the acid from which the ester is derived. When mineral acids are used as hydrolysing agents the rate of hydrolysis appears to be determined largely by the first factor, although the second factor also has an effect, as shown by the fact that ethyl trichloroacetate is hydrolysed more readily than the dichloroacetate. When alkalis are used and also probably when water alone is used, the second factor has a much more marked effect than when acids are used; the effect is so marked in certain cases that the influence of the first factor is almost completely obscured, *e.g.* with the esters of the chloroacetic acids, of the *a*-hydroxy acids and of nitro substituted benzoic acids.

The generalisation drawn by V. Meyer (Ber. 1895, 28, 1263; *cp.* Wegscheider, *ibid.* 2356) viz. that there is a simple relationship between the rate of hydrolysis of an ester by alkalis and its rate of formation by the catalytic method of esterification does not hold. It is highly probable that there may be a relationship between the rate of esterification of an acid by the direct method and the rate of saponification of the ester, and also a relationship between the rate of hydrolysis of the ester by acids and the rate of esterification by the catalytic method. No relationship between the rate of saponification or by hydrolysis by acids and the

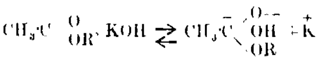
constitution of the alkyl group R′ in the ester $\mathrm{R{\cdot}C}\!<\!\begin{smallmatrix}\mathrm{O}\\ \mathrm{OR'}\end{smallmatrix}$, can be deduced as the data available are not sufficiently numerous.

Since sodium, potassium, and calcium hydroxides as saponifying agents have practically the same effect when solutions of equivalent strengths are used, the conclusion has been drawn that the hydrolysis is due to the hydroxyl ions present. The reaction cannot be a simple addition of the alkali to the ester followed by the elimination of alcohol, as then the reaction with calcium hydroxide would be termolecular

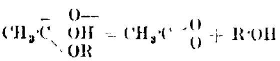
$$2\mathrm{R{\cdot}CO_2Et} + \mathrm{Ca(OH)_2} = \mathrm{(R{\cdot}CO_2)_2Ca} + 2\mathrm{EtOH}$$

whereas it can be shown to be bimolecular.

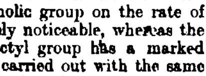
It is possible that the reaction consists in the addition of water (not alkali) to the ester and the subsequent resolution of this complex into acid and alcohol. The alkali in this case would act first as a catalyst, and secondly as a base for neutralising the acid formed. According to Acree (Amer. Chem. J. 1907, 38, 344) the ester can function as a feeble acid and form small amounts of salts with the alkali, *e.g.*



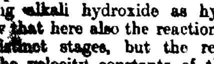
and it is the complex anion which reacts with the water yielding the anion of the acid and alcohol



Esters of dibasic acids. J. Meyer (Zeitsch. physikal. Chem. 1909, 66, 81, and 67, 257) by the study of the hydrolysis of esters of dibasic acids (tartaric, succinic, and camphoric) with hydrochloric acid as catalyst, has been able to prove that the reaction proceeds in two distinct stages: (*a*) normal ester + water → acid ester + alcohol; (*b*) acid ester — water → acid + alcohol. With the ethyl esters of symmetrical dibasic acids, *e.g.* tartaric and succinic, the whole reaction appears to be unimolecular as the velocity constant for the first stage is almost exactly double that for the second stage, and the whole is pseudo-unimolecular. In the case of ethyl camphorate, the ester of an unsymmetrical acid, the two stages proceed at very different rates, the normal ester,



is rapidly hydrolysed to the acid ester,



but this latter is fairly stable, and the method is a convenient one for the preparation of the acid ester. For different esters of the same acid the influence of the alcoholic group on the rate of esterification is scarcely noticeable, whereas the constitution of the actyl group has a marked effect. Experiments carried out with the same esters using alkali hydroxide as hydrolysing agent show that here also the reaction proceeds in two distinct stages, but the relationship between the velocity constants of the two is not so simple as when hydrochloric acid is used. With ethyl malonate the first stage proceeds about 100 times as quickly as the second, but with ethyl succinate the ratio is about 10 : 1, and in neither case can the whole process be represented as a simple bimolecular reaction. With the esters derived from symmetrical dihydric alcohols, *e.g.* glycol diacetate $\mathrm{C_2H_4(OAc)_2}$, although the saponification proceeds in two distinct stages the velocity constants of the two stages bear a simple relationship to one another, *e.g.* 2 : 1, and hence the whole appears to be a bimolecular reaction. The same holds good for the hydrolysis of glyceryl triacetate, where the three distinct stages proceed at the relative rates 3 : 2 : 2.

Esters of sulphonic acids. Esters of sulphonic acids can also be hydrolysed by water, mineral acids, or alkalis, and since most of the sulphonic acids are very strong acids, their esters are hydrolysed quite readily by water alone. The esters are also converted into the corresponding acids when heated with alcohol (Krafft and Roos, Ber. 1892, 25, 2225; Kastle and Murrill, Amer. Chem. J. 1895, 17, 290), a reaction in which an alkyl ether is also formed

$$\mathrm{R{\cdot}SO_2{\cdot}OEt} + \mathrm{EtOH} = \mathrm{R{\cdot}SO_2{\cdot}OH} + \mathrm{Et_2O}$$

This decomposition proceeds slowly at the ordinary temperature, and is brought about more readily by methyl than by ethyl alcohol.

Kastle, Murrill, and Frazer (Amer. Chem. J. 1897, 19, 894) have shown that 0·1 *N*-solutions of sulphuric and acetic acids have no effect on the hydrolysis of esters of sulphonic acids by water. Hydrochloric and hydrobromic acids, on the other hand, have an apparent retarding effect, but this is due to the fact that the halogen hydracids can react with the ester according to the equation:

$$\mathrm{R{\cdot}SO_2{\cdot}OEt} + \mathrm{HCl} \rightleftarrows \mathrm{R{\cdot}SO_2{\cdot}OH} + \mathrm{EtCl}$$

a reaction which does not affect the total acidity of the solution. A more detailed investigation has proved that this second reaction proceeds more rapidly and to a greater extent than the hydrolysis of the ester by water. The hydrolysis of a sulphonic ester by means of a large excess of water or alcohol in acetone solution gives concordant values for K when the equation for a monomolecular reaction is used. Alkalis are much more efficient hydrolysing agents than water for sulphonic esters; this may be due to the alkali acting independently of the water or to the alkali catalytically affecting the hydrolysis by water. The constants at 25° for methyl benzenesulphonate, using water and *N*-potassium hydroxide solution, are 1 : 90 (Wegscheider and Furcht, Monatsh. 1902, 23, 1903). When the neutral ester of a mixed carboxylic sulphonic acid is hydrolysed, *e.g.* $\mathrm{OEt{\cdot}SO_2{\cdot}C_6H_4{\cdot}CO_2Et}$, the $\mathrm{{\cdot}SO_2{\cdot}OEt}$ group is hydrolysed much more readily than the $\mathrm{{\cdot}CO_2Et}$ group, and an acid ester of the type $\mathrm{OH{\cdot}SO_2{\cdot}C_6H_4{\cdot}CO_2Et}$ is formed.

Esters can also be hydrolysed by water with finely divided metals as catalysts, *e.g.* Neilson (Amer. J. physiol. 1903, 10, 191) has shown that platinum black accelerates the hydrolysis of ethyl butyrate by water. The reaction is, however, very slow, and increases with the amount of platinum present. The maximum effect is obtained at 50°, and the activity of the catalyst is readily destroyed by various 'poisons.' The reaction is reversible as platinum

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$$K_{NaOH} : K_{NH_4OH} = 200 : 1.$$

The results obtained by using different esters show that the alkyl group R′ in the ester $\mathrm{R{\cdot}C}\!<\!\begin{smallmatrix}\mathrm{O}\\ \mathrm{OR'}\end{smallmatrix}$ influences the rate of hydrolysis to a greater extent than it does when mineral acids are used for hydrolysing; thus the values for K using sodium hydroxide at 9·4° are: methyl acetate 3·49, ethyl acetate 2·31, propyl acetate 1·92, *iso*butyl acetate 1·62, and *iso*amyl acetate 1·64. The influence of the acyl group R·CO is also marked, as shown by the following values for K at 14·4°, using sodium hydroxide and ethyl esters: acetate 3·2, propionate 2·8, butyrate 1·7, *iso*butyrate 1·73, *iso*valerate 0·62, and benzoate 0·83. Later experiments by Sudborough and Feilmann (Chem. Soc. Proc. 1897, 13, 243) prove that the introduction of methyl groups into the ethyl acetate molecule retards hydrolysis by means of alcoholic potassium hydroxide, whereas the introduction of chlorine atoms facilitates the decomposition. The investigations of Gyr (Ber. 1908, 41, 4308) show that two or three phenyl groups in the ethyl acetate molecule also retard hydrolysis, whereas the ethyl ester of phenylacetic acid is hydrolysed more readily than ethyl acetate itself. The results obtained by Hjelt (Ber. 1896, 29, 1864) with substituted derivatives of ethyl malonate also show that the introduction of an alkyl group into the ethyl malonate molecule retards hydrolysis, and that when two such groups are present the effect is still more noticeable. The influence of the strength of the acid from which the ester is derived also appears to be a determining factor. The investigations of Kellas (Zeitsch. physikal. Chem. 1897, 24, 243) on the hydrolysis of ethyl esters of substituted benzoic acids show that the esters of many substituted benzoic acids are hydrolysed by alcoholic potash more readily than ethyl benzoate itself. This appears to be true of all esters derived from acids much stronger than benzoic acid, *e.g.* the bromo-, chloro-, and nitro-benzoic acids, but does not hold good when the esters are derived from acids with small dissociation constants, *e.g.* the toluic acids. Kellas's results also show that when the rates of hydrolysis of a group of three isomeric esters are compared the ortho-compounds are invariably hydrolysed more slowly than the isomeric, meta-, and para- compounds, even when the ortho- acid is a much stronger acid than the isomers.

Findlay and Turner (Chem. Soc. Trans. 1905, 87, 747) and Findlay and Hickmans (*ibid.* 1909, 95, 1004) show that an *a*-hydroxyl group increases the readiness with which the ester is hydrolysed by alkalis. The ratio K ethyl glycollate : K ethyl acetate = 11·5; and K ethyl lactate : K ethyl propionate = 11·9, and K methyl mandelate : K methyl phenylacetate = 5·7. The introduction of a phenyl group in the *a*-position does not necessarily increase the rate of hydrolysis. The ratio K ethyl phenylacetate : K ethyl acetate = 1·9, but K ethyl mandelate : K ethyl glycollate = 0·88. It is shown that there is no direct proportionality between the affinity constant of the acid and the saponification constant of its ester, although in any given series of compounds the two constants follow the same order. Palomaa (Chem. Soc. Abstr. 1914, i. 136) shows that with esters which contain an oxygen atom in the chain (whether as OH, OR, CO, or O) the velocity of hydrolysis by mineral acids is reduced to a minimum when the oxygen atom is in the *β*-position with respect to the ester group. On the other hand, a cyano group always has a retarding effect on the hydrolysis of an ester by dilute hydrochloric acid, and the effect is more pronounced in the *a*- than in the *β*-position (Amer. J. Sci. 1914, [iv.] 37, 514). Drushel and Dean (*ibid.* 1912, [iv.] 34, 293) show that in the case of acetic acid the rate of hydrolysis is increased by the introduction of the hydroxy group, but retarded by an alkyloxy group. The introduction of hydroxy groups into the butyric acid, on the other hand, had a retarding effect (Dean, *ibid.* 1914, [iv.] 37, 331). For hydrolysis of halogenated esters, *see* Drushel, *ibid.* 1912, [iv.] 34, 69; for hydroxy and alkyloxy derivatives of propionic acid, *ibid.* 1913, [iv.] 35, 486. When alkali is used for hydrolysing the esters of hydroxy acids (*ibid.* 905) the esters derived from strong acids are more readily saponified than those from weak. The results obtained by different authorities point to the general conclusion that two factors at least determine the rate of hydrolysis of ethyl esters by alkalis or acids. (*a*) The complexity of the acyl group, especially as regards the presence of substituents in close proximity to the carbonyl group, *e.g.* in the *a*-position in aliphatic, the ortho- position in aromatic, and probably the cis- position in unsaturated esters. (*b*) The strength of the acid from which the ester is derived. When mineral acids are used as hydrolysing agents the rate of hydrolysis appears to be determined largely by the first factor, although the second factor also has an effect, as shown by the fact that ethyl trichloroacetate is hydrolysed more readily than the dichloroacetate. When alkalis are used and also probably when water alone is used, the second factor has a much more marked effect than when acids are used; the effect is so marked in certain cases that the influence of the first factor is almost completely obscured, *e.g.* with the esters of the chloroacetic acids, of the *a*-hydroxy acids and of nitro substituted benzoic acids.

The generalisation drawn by V. Meyer (Ber. 1895, 28, 1263; *cp.* Wegscheider, *ibid.* 2356) viz. that there is a simple relationship between the rate of hydrolysis of an ester by alkalis and its rate of formation by the catalytic method of esterification does not hold. It is highly probable that there may be a relationship between the rate of esterification of an acid by the direct method and the rate of saponification of the ester, and also a relationship between the rate of hydrolysis of the ester by acids and the rate of esterification by the catalytic method. No relationship between the rate of saponification or by hydrolysis by acids and the

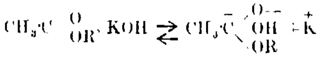
constitution of the alkyl group R′ in the ester $\mathrm{R{\cdot}C}{<}^{\mathrm{O}}_{\mathrm{OR'}}$, can be deduced as the data available are not sufficiently numerous.

Since sodium, potassium, and calcium hydroxides as saponifying agents have practically the same effect when solutions of equivalent strengths are used, the conclusion has been drawn that the hydrolysis is due to the hydroxyl ions present. The reaction cannot be a simple addition of the alkali to the ester followed by the elimination of alcohol, as then the reaction with calcium hydroxide would be termolecular

$$\mathrm{2R{\cdot}CO_2Et + Ca(OH)_2 = (R{\cdot}CO_2)_2Ca + 2EtOH}$$

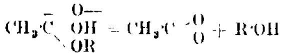
whereas it can be shown to be bimolecular.

It is possible that the reaction consists in the addition of water (not alkali) to the ester and the subsequent resolution of this complex into acid and alcohol. The alkali in this case would act first as a catalyst, and secondly as a base for neutralising the acid formed. According to Acree (Amer. Chem. J. 1907, 38, 344) the ester can function as a feeble acid and form small amounts of salts with the alkali, *e.g.*



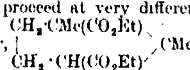
$$\mathrm{CH_3{\cdot}C}\begin{matrix}\mathrm{O}\\ \mathrm{OR}\end{matrix} + \mathrm{KOH} \rightleftarrows \mathrm{CH_3{\cdot}\overset{-}{C}}\begin{matrix}\mathrm{O-}\\ \mathrm{OH}\\ \mathrm{OR}\end{matrix} + \overset{+}{\mathrm{K}}$$

and it is the complex anion which reacts with the water yielding the anion of the acid and alcohol



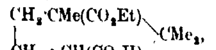
$$\mathrm{CH_3{\cdot}\overset{-}{C}}\begin{matrix}\mathrm{O-}\\ \mathrm{OH}\\ \mathrm{OR}\end{matrix} = \mathrm{CH_3{\cdot}C}\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix} + \mathrm{R{\cdot}OH}$$

Esters of dibasic acids. J. Meyer (Zeitsch. physikal. Chem. 1909, 66, 81, and 67, 257) by the study of the hydrolysis of esters of dibasic acids (tartaric, succinic, and camphoric) with hydrochloric acid as catalyst, has been able to prove that the reaction proceeds in two distinct stages: (*a*) normal ester + water → acid ester + alcohol; (*b*) acid ester — water → acid + alcohol. With the ethyl esters of symmetrical dibasic acids, *e.g.* tartaric and succinic, the whole reaction appears to be unimolecular as the velocity constant for the first stage is almost exactly double that for the second stage, and the whole is pseudo-unimolecular. In the case of ethyl camphorate, the ester of an unsymmetrical acid, the two stages proceed at very different rates, the normal ester,



$$\begin{matrix}\mathrm{CH_2{\cdot}CMe(CO_2Et)}\\ |\\ \mathrm{CH_2{\cdot}CH(CO_2Et)}\end{matrix}\!\!>\!\mathrm{CMe_2},$$

is rapidly hydrolysed to the acid ester,



$$\begin{matrix}\mathrm{CH_2{\cdot}CMe(CO_2Et)}\\ |\\ \mathrm{CH_2{\cdot}CH(CO_2H)}\end{matrix}\!\!>\!\mathrm{CMe_2},$$

but this latter is fairly stable, and the method is a convenient one for the preparation of the acid ester. For different esters of the same acid the influence of the alcoholic group on the rate of esterification is scarcely noticeable, whereas the constitution of the actyl group has a marked effect. Experiments carried out with the same esters using alkali hydroxide as hydrolysing agent show that here also the reaction proceeds in two distinct stages, but the relationship between the velocity constants of the two is not so simple as when hydrochloric acid is used. With ethyl malonate the first stage proceeds about 100 times as quickly as the second, but with ethyl succinate the ratio is about 10 : 1, and in neither case can the whole process be represented as a simple bimolecular reaction. With the esters derived from symmetrical dihydric alcohols, *e.g.* glycol diacetate $\mathrm{C_2H_4(OAc)_2}$, although the saponification proceeds in two distinct stages the velocity constants of the two stages bear a simple relationship to one another, *e.g.* 2 : 1, and hence the whole appears to be a bimolecular reaction. The same holds good for the hydrolysis of glyceryl triacetate, where the three distinct stages proceed at the relative rates 3 : 2 : 2.

Esters of sulphonic acids. Esters of sulphonic acids can also be hydrolysed by water, mineral acids, or alkalis, and since most of the sulphonic acids are very strong acids, their esters are hydrolysed quite readily by water alone. The esters are also converted into the corresponding acids when heated with alcohol (Krafft and Roos, Ber. 1892, 25, 2225; Kastle and Murrill, Amer. Chem. J. 1895, 17, 290), a reaction in which an alkyl ether is also formed

$$\mathrm{R{\cdot}SO_2{\cdot}OEt + EtOH = R{\cdot}SO_2{\cdot}OH + Et_2O}$$

This decomposition proceeds slowly at the ordinary temperature, and is brought about more readily by methyl than by ethyl alcohol.

Kastle, Murrill, and Frazer (Amer. Chem. J. 1897, 19, 894) have shown that 0·1 *N*-solutions of sulphuric and acetic acids have no effect on the hydrolysis of esters of sulphonic acids by water. Hydrochloric and hydrobromic acids, on the other hand, have an apparent retarding effect, but this is due to the fact that the halogen hydracids can react with the ester according to the equation:

$$\mathrm{R{\cdot}SO_2{\cdot}OEt + HCl \rightleftarrows R{\cdot}SO_2{\cdot}OH + EtCl}$$

a reaction which does not affect the total acidity of the solution. A more detailed investigation has proved that this second reaction proceeds more rapidly and to a greater extent than the hydrolysis of the ester by water. The hydrolysis of a sulphonic ester by means of a large excess of water or alcohol in acetone solution gives concordant values for K when the equation for a monomolecular reaction is used. Alkalis are much more efficient hydrolysing agents than water for sulphonic esters; this may be due to the alkali acting independently of the water or to the alkali catalytically affecting the hydrolysis by water. The constants at 25° for methyl benzenesulphonate, using water and *N*-potassium hydroxide solution, are 1 : 90 (Wegscheider and Furcht, Monatsh. 1902, 23, 1903). When the neutral ester of a mixed carboxylic sulphonic acid is hydrolysed, *e.g.* $\mathrm{OEt{\cdot}SO_2{\cdot}C_6H_4{\cdot}CO_2Et}$, the $\mathrm{{\cdot}SO_2{\cdot}OEt}$ group is hydrolysed much more readily than the $\mathrm{{\cdot}CO_2Et}$ group, and an acid ester of the type $\mathrm{OH{\cdot}SO_2{\cdot}C_6H_4{\cdot}CO_2Et}$ is formed.

Esters can also be hydrolysed by water with finely divided metals as catalysts, *e.g.* Neilson (Amer. J. physiol. 1903, 10, 191) has shown that platinum black accelerates the hydrolysis of ethyl butyrate by water. The reaction is, however, very slow, and increases with the amount of platinum present. The maximum effect is obtained at 50°, and the activity of the catalyst is readily destroyed by various 'poisons.' The reaction is reversible as platinum

Reicher's experiments were carried out at 9·4°, and show that the velocity is practically the same whether sodium, potassium, or calcium hydroxide is used as saponifying agent. With strontium or barium hydroxide the velocity constants are somewhat smaller and with a feeble alkali, such as ammonium hydroxide, the value for K is much less, *e.g.*

$$K_{\mathrm{NaOH}} : K_{\mathrm{NH_4OH}} = 200 : 1.$$

The results obtained by using different esters show that the alkyl group R′ in the ester $\mathrm{R{\cdot}C}{<}^{\mathrm{O}}_{\mathrm{OR'}}$ influences the rate of hydrolysis to a greater extent than it does when mineral acids are used for hydrolysing; thus the values for K using sodium hydroxide at 9·4° are: methyl acetate 3·49, ethyl acetate 2·31, propyl acetate 1·92, *iso*butyl acetate 1·62, and *iso*amyl acetate 1·64. The influence of the acyl group R·CO is also marked, as shown by the following values for K at 14·4°, using sodium hydroxide and ethyl esters: acetate 3·2, propionate 2·8, butyrate 1·7, *iso*butyrate 1·73, *iso*valerate 0·62, and benzoate 0·83. Later experiments by Sudborough and Feilmann (Chem. Soc. Proc. 1897, 13, 243) prove that the introduction of methyl groups into the ethyl acetate molecule retards hydrolysis by means of alcoholic potassium hydroxide, whereas the introduction of chlorine atoms facilitates the decomposition. The investigations of Gyr (Ber. 1908, 41, 4308) show that two or three phenyl groups in the ethyl acetate molecule also retard hydrolysis, whereas the ethyl ester of phenylacetic acid is hydrolysed more readily than ethyl acetate itself. The results obtained by Hjelt (Ber. 1896, 29, 1864) with substituted derivatives of ethyl malonate also show that the introduction of an alkyl group into the ethyl malonate molecule retards hydrolysis, and that when two such groups are present the effect is still more noticeable. The influence of the strength of the acid from which the ester is derived also appears to be a determining factor. The investigations of Kellas (Zeitsch. physikal. Chem. 1897, 24, 243) on the hydrolysis of ethyl esters of substituted benzoic acids show that the esters of many substituted benzoic acids are hydrolysed by alcoholic potash more readily than ethyl benzoate itself. This appears to be true of all esters derived from acids much stronger than benzoic acid, *e.g.* the bromo-, chloro-, and nitro-benzoic acids, but does not hold good when the esters are derived from acids with small dissociation constants, *e.g.* the toluic acids. Kellas's results also show that when the rates of hydrolysis of a group of three isomeric esters are compared the ortho-compounds are invariably hydrolysed more slowly than the isomeric, meta-, and para- compounds, even when the ortho- acid is a much stronger acid than the isomers.

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complicated by the fact that it is impossible to isolate, in a state of purity, the particular enzyme required, and it may be accompanied by another enzyme capable of causing the destruction (autolysis) of the first, and thus bringing the reaction to an end long before all the substrate is decomposed.

The name given to a particular hydrolysing enzyme usually indicates the substance it is capable of hydrolysing and in all cases the termination *ase* is used. Thus maltase is the enzyme which hydrolyses maltose, amylase the enzyme which hydrolyses starch; but in some cases older names which were in use before this scheme was adopted, are still retained, *e.g.* sucrase, the enzyme which inverts sucrose (cane sugar), is still called invertase or even invertin, the common digestive enzymes are termed trypsin and pepsin. The substance which is decomposed by the enzyme is usually termed the substrate.

Although the processes of hydrolysis by acids and by enzymes are frequently compared it should be borne in mind that the rate at which a given substance is hydrolysed by the two different types of catalysts is frequently quite different, *e.g.* sucrose is hydrolysed by invertase much more readily than by a N-solution of hydrochloric acid; in fact, with a concentrated solution of invertase at 0° the inversion is practically instantaneous. It is not essential that the products obtained by the two processes should be identical. Thus in the case of the inversion of cane sugar by invertase the products are α-glucose and α-fructose, whereas when mineral acids are used the products are equilibrium mixtures of α- and β-glucose and α- and β-fructose, as the α-glucose and the α-fructose undergo immediate mutarotation in the presence of the mineral acid. Another example of a similar type is met with in the tri-saccharose, raffinose; when hydrolysed by acids this yields galactose, fructose, and glucose, the same sugar with raffinase yields melibiose and fructose, and with emulsin it yields galatose and sucrose. Similarly natural products of protein character yield comparatively simple amino acids when hydrolysed with acids or alkalis, whereas with enzymes more complex intermediate products are formed.

An important point of difference between hydrolysis by means of acids or alkalis and hydrolysis under the influence of enzymes is that any particular enzyme has a very restricted use as a catalyst or the action of enzymes is essentially selective. Thus lipase can hydrolyse esters and not carbohydrates; maltase can hydrolyse maltose but not sucrose. That a slight difference in the configuration of two isomeric compounds is sufficient to affect their reactivities with a particular enzyme is shown in the case of the two stereoisomeric α-methylglucosides. (For further details, *see* art. FERMENTATION.) Further examples are met with among the numerous polypeptides prepared within recent years (*cp.* Fischer and Bergell, Ber. 1903, 36, 2592; 1904, 37, 3103; Fischer and Abderhalden, Zeitsch. physiol. Chem. 1905, 46, 52; 1907, 51, 264).

The behaviour of some of the natural and artificial glucosides (*see* GLUCOSIDES) towards the two enzymes maltase and emulsin has been made use of in determining their configurations. Thus maltose, which is hydrolysed by maltase but not by emulsin, is regarded as an anhydride of α-glucose, having a configuration similar to that of the α-methylglucoside; most of the natural glucosides, on the other hand, are hydrolysed by emulsin, but not by maltase, and therefore are probably analogous to β-methylglucoside. As a rule a natural glucoside is accompanied in the plant tissue by the enzyme which is able to hydrolyse it. The commonest glucosidoclastic enzymes, *i.e.* enzymes capable of hydrolysing glucosides are emulsin (β-glucase), myrosin, which hydrolyses sulphur glucosides, rhamnase, and tannase.

The products formed by the hydrolysis of naturally occurring compounds by enzymes are various; thus the natural glucosides can give rise to sugars, alcohols, phenols, aldehydes, acids, mustard oils, anthracene derivatives, indigo, &c.

It has been proved in many cases that a specific enzyme can act not merely as a hydrolysing, but also as a synthesising agent. The process of hydrolysis is thus, in certain cases, a balanced reaction, but the equilibrium is mainly in the direction of analysis and not synthesis. The synthesising activity of an enzyme was first demonstrated by Croft Hill (Chem. Soc. Trans. 1898, 73, 634; 1903, 83, 578) in the case of maltase. The greater portion of the maltose is hydrolysed by the enzyme to glucose, but a certain proportion of di-saccharose is always present.

A series of alkyl-β-glucosides and galactosides has been synthesised by Bourquelot using emulsin or α-glucosides by an enzyme extracted from bottom yeast by means of water (Ann. Chim. 1913 [viii.], 29, 145; 1915 [ix.], 3, 287; 1915 [ix.], 4, 310; *cp.* also Bayliss, J. physiol. 1913, 46, 236).

Bayliss has synthesised arbutin from quinol and dextrose by means of emulsin in the presence of glycerol (Chem. Soc. Abs. 1912, 1, 328) The synthetic action of enzymes in forming polypeptides and proteins has also been demonstrated (Abderhalden, Chem. Soc. Abs. 1915, 1, 725).

According to Bayliss (J. physiol. 1915, 50, 85) the reaction occurs at the interface of contact between the solid enzyme phase and the liquid substrate phase, as when many of them are filtered the filtrate is inactive, but the solid active.

Emulsin and lipase have also been shown to possess synthesising properties; in the latter case natural fats have been synthesised by the action of lipases on mixtures of glycerol and the higher fatty acids in the absence of a large excess of water. The lipatic enzymes present in certain seeds are made use of on a commercial scale for the preparation of fatty acids from natural fats (*cp.* Welter, Zeitsch. angew. Chem. 1911, 24, 385; Pottevin, Bull. Soc. chim. 1906, [iii.] 35, 693). For details of the synthetic functions of enzymes, *see* art. FERMENTATION.

In some of these balanced actions between carbohydrates or esters and enzymes it has been shown that the equilibrium mixture is the same, whether mineral acid or enzyme is used, *e.g.* Visser's experiments using invertase and emulsin;

in other cases, however, the equilibrium mixture with the enzyme is quite different from that obtained when an acid is used, *e.g.* Dietz's experiments with lipase and *iso*-amyl *n*-butyrate (Zeitsch. physiol. Chem. 1907, 52, 279).

A considerable amount of work has been done on the velocities of different reactions in which enzymes play a part. Henri (Lois general de l'action des diastases, 1903) and others claim that the rate of inversion of sucrose by invertase, unlike that by mineral acids, does not agree with the unimolecular formula. The investigations of O'Sullivan and Tompson (Chem. Soc. Trans. 1890, 57, 834) and of Hudson (J. Amer. Chem. Soc. 1908, 30, 1160, 1564; 1909, 31, 655) prove conclusively that the unimolecular formula holds for any given solution, if the birotation of the *a*-glucose and *a*-fructose first formed is taken into consideration. The complications attending the mutarotation of the glucose and fructose can be avoided by adding a small amount of alkali, *e.g.* 10 c.c. of 0·4 *N*-sodium carbonate solution for each 100 c.c. of sugar solution, a short time before the polarimetric reading is taken. The alkali stops the hydrolysis and rapidly brings about equilibrium between the *a*- and *β*-glucoses and *a*- and *β*-fructoses, so that the normal rotatory power of invert sugar is given. Hudson's results clearly prove that the *a*-modifications of glucose and fructose are first formed, and that these are stable in the presence of enzyme, but rapidly undergo mutarotation in the presence of a little alkali. Hudson's experiments also show that a trace of hydrochloric acid, *e.g.* 0·0006 *N*-, accelerates the action of the invertase to an appreciable extent.

The decomposition of the cane sugar is directly proportional to the concentration of the enzyme, and in very dilute solutions (under 5 p.c.) is also proportional to the concentration of the sugar, but with more concentrated solutions it is not even approximately proportional, but decreases and becomes practically zero in the strongest solutions. According to O'Sullivan and Tompson, and to Hudson, the diminution in the velocity in concentrated solutions is due principally to the viscosity of the medium; it may also be partly due to the formation of a definite compound between the sugar and enzyme. According to A. J. Brown (Chem. Soc. Trans. 1902, 81, 373) a given quantity of invertase decomposes a nearly constant weight of sugar in unit time (*i.e.* the decomposition is independent of the sugar concentration), provided the solution is moderately concentrated; but after an appreciable amount of sugar is decomposed the further inversion is directly proportional to the concentration of the sugar. This change of velocity from a linear to a logarithmic period is in harmony with the view that the sugar unites with the enzyme, and that it is the additive compound which is hydrolysed, and that the enzyme thus liberated immediately combines with a further amount of sugar. *Cp.* the hydrolysis of milk sugar by enzymes (E. F. Armstrong, Proc. Roy. Soc. 1904, 73, 500).

The reaction between salicin and water in the presence of emulsin is also a unimolecular reaction (Hudson and Paine, J. Amer. Chem. Soc. 1909, 31, 1242), provided alkali is added to bring about mutarotation of the *β*-glucose, which is the primary product

$$C_{13}H_{18}O_7+H_2O=C_6H_{12}O_6+\underset{\text{Salicyl alcohol.}}{C_7H_8O_2}$$

The ester splitting enzyme contained in castor seeds is probable a mixture of two distinct enzymes: (*a*) an esterase which is soluble in water and which hydrolyses ethyl butyrate more readily than glyceryl esters; (*b*) a true lipase which is almost insoluble in water and which hydrolyses glyceryl esters more readily than ethyl butyrate (Falk and Sugiura, J. Amer. Chem. Soc. 1913, 35, 1904; 1915, 37, 217).

The reaction between lipase and *iso*amyl butyrate or between the same enzyme and *iso*amyl alcohol and *n*-butyric acid in the presence of a large excess of alcohol is a normal unimolecular reaction, although it proceeds in a heterogeneous medium. Dietz concludes that the reaction takes place in the solid phase, and that the diffusion of the ester or acid into the colloidal enzyme takes place so rapidly when compared with the velocity of reaction that the rates of diffusion do not affect the determination of the velocity of the reaction.

The hydrolysis of ethyl butyrate by lipase (Pierce, J. Amer. Chem. Soc. 1910, 32, 1517) points to the formation of an additive compound of the ester and enzyme. In many other cases the velocity relationships are not so simple. In some of these the reaction is retarded after a certain time owing to the product or products formed combining with the enzyme, or to negative autocatalysis, or to the gradual destruction of the enzyme.

In the reaction between pepsin and albumen the amount of albumen transformed in given time by different amounts of pepsin is proportional to the square root of the pepsin concentrations. The same relationship holds good with regard to trypsin and albumen, and is due to the fact that the velocity is inversely proportional to the amount of substance transformed, and this points to the formation of a definite compound between the enzyme and one of the products.

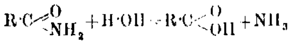
Most decompositions by enzymes are characterised by a high temperature coefficient when compared with catalytic reactions in which acid or alkali is used. In the latter case the coefficient is about 2–3 for a rise of 10°; with emulsin, however, the coefficient is 7·14 for a rise from 60° to 70°, with trypsin 5·3 for a rise from 20° to 30°; but like most colloidal catalysts enzymes exhibit an optimum temperature, at which the activity is greatest, and then falls again with further rise of temperature. This may be due to the coagulating effects which a moderately high temperature usually has on the majority of colloids.

In certain cases it has been found possible to obtain by dialysis from a given enzyme two portions, a dialysate and a residue; neither portion alone is active, but the hydrolytic activity is restored when the dialysate is added to the dialysed residue. This residue is decomposed when boiled with water, and is the enzyme proper, whereas the dialysate is not decomposed when boiled and contains the co-enzyme (*see* art. FERMENTATION). In the case of liver lipases it has been proved that both enzyme and co-enzyme are essential for the hydrolysis of esters, and it has also been proved that the co-enzyme is a metallic salt of taurocholic acid. In living tissues a number of complex substances are present which are capable of interfering with the specific action of an enzyme. These are termed anti-enzymes; some are normally present in tissues, others appear to be formed when an enzyme is injected into the tissue.

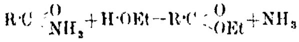
A view generally held with regard to the mechanism of enzyme reaction is that compounds perhaps of the type of 'absorption compounds' (Bayliss) are formed between the enzyme and substrate, and that the absorbed material then reacts with water (*see* art. FERMENTATION). The fact that a specific enzyme can hydrolyse only certain particular substrates is in harmony with this view, as it is known that chemical constitution plays an important part in absorption phenomena (Zung, Arch. inter. Physiol. 1907, 5, 245; Hedin, Bio-Chem. J. 1907, 2, 112; Aeree, J. Amer. Chem. Soc. 1908, 30, 1755; *cp.* also Freundlich, Zeitsch. physikal. Chem. 1907, 57, 385).

6. **Alcoholysis.** Reactions in which alcohols play much the same part as water in hydrolysis are usually grouped together under the name alcoholysis. The reaction with methyl alcohol is termed '*methanolysis*,' and that with ethyl '*ethanolysis*.'

The ethanolysis of an acid amide in the presence of a mineral acid is analogous to the hydrolysis of the amide by dilute mineral acids as shown by the two equations:



$$R{\cdot}C{<}^{O}_{NH_2}+H{\cdot}OH=R{\cdot}C{<}^{O}_{OH}+NH_3$$



$$R{\cdot}C{<}^{O}_{NH_2}+H{\cdot}OEt=R{\cdot}C{<}^{O}_{OEt}+NH_3$$

The latter reaction has been studied in detail by Reed (Amer. Chem. J. 1909, 41, 483). The reaction is bimolecular as the catalyst is gradually neutralised by the ammonia formed in the reaction, and proceeds at an easily measurable rate at 50° in the case of benzamide. A comparison of the values of K for *p*- and *m*-nitrobenzamide shows that this is 1·16, a value practically identical with the ratio for the hydrolysis of the two amides. The ratio of the constants for benzamide and *m*-nitrobenzamide varies considerably with the concentration of the hydrogen chloride. The presence of small amounts of water on the rate of alcoholysis is also marked, just as in the case of the esterification of an acid, and similarly ortho-substituents appear to have inhibiting effects. The general conclusion drawn is that the mechanism of alcoholysis is analogous to that of hydrolysis, and consists in the formation of salts between the amide and the mineral acid and the reaction of the complex cation with the alcohol.

Another common type of alcoholysis met with is the conversion of an ester of a given acid into another ester of the same acid by means of an alcohol, *e.g.*:

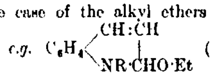
$$R{\cdot}CO{\cdot}OEt+MeOH\rightleftarrows R{\cdot}CO{\cdot}OMe+EtOH$$

This change does not take place readily except in the presence of a catalyst, the most efficient being sodium alkyl oxide (Purdie, Chem. Soc. Trans. 1885, 47, 862; 1887, 51, 627; 1888, 53, 391; Claisen, Ber. 1887, 20, 646), hydrogen chloride (Patterson and Dickinson, Chem. Soc. Trans. 1901, 79, 280), sodium hydroxide (Henriques, Zeitsch. angew. Chem. 1898, 338; Pfannl. Monatsh. 1910, 31, 301; Kommenos, *ibid.* 1910, 31, 111, 687; 1911, 32, 77; Kremann, *ibid.* 1905, 26, 783; 1908, 29, 23) or ammonia (Leuchs and Theodorescu, Ber. 1910, 43, 1239). As a rule only a small amount of the catalyst need be used, but with the esters of aromatic acids saturation with hydrogen chloride is necessary. The reaction appears to be reversible, as it is possible to transform an ethyl into a methyl and conversely a methyl into an ethyl ester. The reaction is not limited to methyl and ethyl esters, but can be applied to more complex esters, such as benzyl and phenyl, and also to glyceryl esters (*cp.* Haller, Compt. rend. 1906, 143, 657; 1908, 146, 259; Fanto and Stritar, Monatsh. 1908, 29, 299), and is a most convenient laboratory method for the conversion of a given ester into another ester derived from the same acid. The esters of the great majority of aliphatic and aromatic acids react in this manner, but Sudborough and Edwards have shown that when the esters are derived from diortho-substituted benzoic acids the transformation cannot be affected by using either sodium alkyl oxide or saturating with hydrogen chloride and boiling for some time. Even when several substituents are present transformation occurs, provided the ortho- positions are free. This indicates that the transformation of esters under the influence of hydrogen chloride is analogous to the esterification of an acid by the same catalyst.

This analogy has been further confirmed by determining the rates of alcoholysis of various esters. These changes cannot be measured by a simple chemical method as in the case of esterification or hydrolysis, but use has been made of the volume changes which occur and the results obtained by dilatometric readings at constant temperature indicate that with an excess of the alcohol and using hydrogen chloride as catalyst the reaction

$$MeOH+R{\cdot}CO_2Et\rightarrow EtOH+R{\cdot}CO_2Me$$

is practically unimolecular. The steric effects are very similar to those met with in the case of catalytic esterification (Kolhatkar, Chem. Soc. Trans. 1915, 107, 921). (*See* ESTERIFICATION.)

Similar transformations can be brought about in the case of the alkyl ethers of carbonium bases, *e.g.*  $C_6H_4{<}\begin{array}{l}CH{:}CH\\ \quad\ \ |\\ NR{\cdot}CHO{\cdot}Et\end{array}$ (Decker, J. pr. Chem. 1890, [ii.] 45, 182), and of the oxygen ethers of substituted thiocarbamides, *e.g.*

$$OEt{\cdot}CH_2{\cdot}NH{\cdot}CS{\cdot}NHPh \rightarrow OMe{\cdot}CH_2{\cdot}NH{\cdot}CS{\cdot}NHPh$$

(Johnson and Guest, J. Amer. Chem. Soc. 1910, 32, 1279). Comp. also Kuntze (Arch. Pharm. 1908, 246, 110). An interesting case of alcoholysis observed by Willstätter and Stoll (Annalen, 1910, 378, 18) is the conversion of amorphous chlorophyll into crystalline chlorophyll by ethyl alcohol in the presence of an enzyme 'chlorophyllase,' which accompanies chlorophyll in plant tissues. The reaction consists in the replacement of the complex phytyl group by the simpler ethyl group

$$CO_2H\cdot C_{31}H_{29}N_4Mg(CO_2Me)(CO_2C_{20}H_{39}) + EtOH$$
$$= C_{20}H_{39}OH + CO_2H\cdot C_{31}H_{29}N_4Mg(CO_2Me)(CO_2Et)$$

For alcoholysis of acid amides and thioamides using mercaptans instead of alcohols, *see* Reed, Chem. Soc. Abstr. 1913, 1, 975.

J. J. S.

HYDROMAGNESITE. Hydrated basic carbonate of magnesium, $3MgCO_3\cdot Mg(OH)_2\cdot 3H_2O$, occurring as small, acicular, or bladed (orthorhombic or monoclinic) crystals, but more often as white, earthy, or chalky masses. It is a mineral of secondary origin, and usually occurs as veins in serpentine, from which it has been derived. It is softer and less heavy (sp.gr. 2·16) than magnesite. When calcined it can be used for the same purposes as magnesite (*q.v.*). A large deposit is quarried at Atlin, in British Columbia (for analyses, *see* G. A. Young, Sum. Rep. Geol. Survey, Canada, 1915); and there is a considerable quantity available at a spot 93 miles north of Ashcroft, in the Lillooet district of British Columbia. Several occurrences are known in California. It is also found with the massive magnesite of Eubœa in Greece.

L. J. S.

HYDROMETER *v.* SPECIFIC GRAVITY.

HYDROPHANE *v.* OPAL.

HYDROPYRIN. A trade name for sodium acetylsalicylate. *v.* SYNTHETIC DRUGS.

HYDROQUINONE, HYDROTOLUQUINONE *v.* PHENOL AND ITS HOMOLOGUES.

HYDROQUINONE CARBOXYLIC ACID *v.* PROTOCATECHUIC ACID.

HYDROSOLS *v.* COLLOIDS.

HYDROSULPHITES *v.* SULPHUR.

HYDROXYACETOPHENONES *v.* KETONES.

HYDROXY ACIDS. *Oxy acids.* The organic hydroxy acids are derived from the corresponding non-hydroxylated acids by the replacement of one or more hydrogen atoms in the hydrocarbon radicle of the acid by the same number of hydroxyl groups. According as the hydroxyl group is introduced into a fatty radicle or into a benzenoid radicle, the resulting acid is an alcohol-acid or a phenol-acid.

HYDROXY ACIDS OF THE ALIPHATIC SERIES.

There are several groups of hydroxy acids of the aliphatic series and these will be discussed *seriatim*.

I. Monohydroxymonocarboxylic acids

$C_nH_{2n}<^{OH}_{CO_2H}$. The most important members of this group are glycollic, lactic, hydracrylic, hydroxybutyric, and hydroxystearic acids (*q.v.*). They occur naturally, *e.g.* glycollic acid in unripe grapes and in the leaves of *Ampelopsis* (*Vitis*) *hederacea* (D. C.), lactic acid in the juice of the muscles, in sour milk, in pickles and in the gastric juice.

General methods of preparation.

(i) By the careful oxidation of diprimary, primary secondary, and primary tertiary glycols with dilute nitric acid or with platinum black and air, *e.g.* lactic acid from glycol.

(ii) By the reduction of aldehyde acids, keto-acids, and dicarboxylic acids with sodium amalgam or with zinc and hydrochloric or sulphuric acids, *e.g.* lactic acid from pyroracemic acid and glycollic acid from oxalic acid.

(iii) By boiling monohalogen fatty acid with silver oxide, alkali, or with water or by distilling them, *e.g.* glycollic acid from monochloroacetic acid; hydracrylic acid from *β*-chloropropionic acid; *γ*-butyrolactone from *γ*-chlorobutyric acid.

(iv) By the action of nitrous acid on amino acids of the fatty series, *e.g.* glycollic acid from glycine.

(v) By the action of hydrogen cyanide followed by hydrochloric acid on aldehydes, ketones, and glycolchlorhydrins, *e.g.* lactic acid from acetaldehyde; hydracrylic acid from glycolchlorhydrin.

(vi) By treating unsaturated acids with hydrobromic acid, or with dilute sulphuric acid or by distilling them, *e.g.* *γ*-valerolactone from allylacetic acid.

Properties.—These acids may be subdivided into three groups, primary, secondary, and tertiary acids, *e.g.* hydracrylic acid, $CH_3(OH)\cdot C<^{H}_{H}CO_2H$, lactic acid, $CH_3\cdot C<^{H}_{OH}CO_2H$ and *a*-hydroxy*iso*butyric acid, $CH_3\cdot C<^{CH_3}_{OH}COOH$. They also exhibit differences in their properties depending on the position of the hydroxyl group in the molecule, *i.e.* whether they are *a*-, *β*- or *γ*-hydroxy-acids. They are more soluble in water, but less soluble in ether than the corresponding fatty acids. They are also less volatile and, as a rule, cannot be distilled unchanged.

General reactions.

(i) Like the fatty acids they yield through change in the carboxyl group normal salts, esters, amides, and nitriles.

(ii) Like the alcohols, the hydrogen of the hydroxyl group may be replaced by alkali metals or by alkyl groups; also by the action of acyl chlorides or of a mixture of concentrated nitric and sulphuric acids, acid radicles or the nitro group may be substituted for it.

(iii) Phosphorus pentachloride replaces the two hydroxyl groups by chlorine, *e.g.* glycollic acid yields chloracetylchloride.

(iv) Hydriodic acid reduces the hydroxy acids to the corresponding fatty acids, *e.g.* propionic acid from lactic acid.

In the above reactions the hydroxy acids behave similarly, but on oxidation or by the application of heat, these acids show great differences.

(v) On oxidation these acids yield different products, according to whether they are primary, secondary, or tertiary acids.

(*a*) Primary acids yield aldehyde acids and dibasic acids, *e.g.* glycollic acid yields glyoxylic and oxalic acids.

(*b*) Secondary acids yield ketonic acids; the *a*-ketonic acids change to aldehyde and carbon dioxide, the *β*-ketonic acids to ketones and carbon dioxide, *e.g.* lactic acid yields pyruvic acid, which changes into acetaldehyde and carbon dioxide.

(*c*) Tertiary *a*-hydroxy acids yield ketones, *e.g.* *a*-hydroxy*iso*butyric acid yields acetone.

(vi) By the application of heat, differences in deportment are shown by these acids, according as they are α-, β-, or γ-hydroxy acids.

(*a*) α-Hydroxy acids lose water and become cyclic double esters—the lactides, *e.g.* lactic acid becomes lactide, two molecules of the acid condensing with the loss of two molecules of water.

(*b*) β-Hydroxy acids lose water and become unsaturated acids, *e.g.* hydracrylic acid becomes acrylic acid.

(*c*) γ- and δ-Hydroxy acids lose water at the ordinary temperature and change more or less completely into simple cyclic esters—lactones.

II. **Aldehyde acids.** Formic acid is the simplest member of this group of acids, and also of the fatty acid series. The next member is glyoxylic acid, $CHO{\cdot}CO_2H$. Its claim to be considered here lies in the fact that all the salts are derived from the dihydroxy formula of glyoxylic acid $(OH)_2CH{\cdot}CO_2H$, and thus it behaves both as an aldehyde acid and as a dihydroxy acid. For details as to this group of acids *v.* GLYOXYLIC ACID.

III. **Monohydroxydicarboxylic acids**

$$C_nH_{2n-1}(OH)(CO_2H)_2$$

Various groups of monohydroxydicarboxylic acids are known, corresponding to the several groups of dibasic acids (*q.v.*). The most important acids of this type are tartronic, malic, α-glutanic and paraconic acids. They occur in nature; thus malic acid in unripe gooseberries, and in rhubarb; α-hydroxyglutaric acid in molasses. The acids in which the hydroxyl group occupy the γ position with reference to the carboxyl group, when separated from their salts, readily part with water and become lactones, *e.g.* paraconic acid. The methods of preparation are very similar to those of the monobasic acids.

IV. **Dihydroxydicarboxylic acids.** The most important acid of this group is tartaric acid (*q.v.*). Mesoxalic acid, which is ketomalonic acid, exhibits tautomerism and behaves both as a keto-acid and as a dihydroxy acid.

V. **Hydroxytricarboxylic acids.** The most important acid of this group is citric acid (*q.v.*).

HYDROXY ACIDS OF THE AROMATIC SERIES.

If the hydroxyl group is attached to the benzene nucleus of a carboxy acid derived from benzene or its homologues, the acid thus formed is a phenol acid. Examples of this class are the three isomeric hydroxybenzoic acids, which have the formula $C_6H_4(OH)COOH$. On the other hand, in the case of carboxy acids derived from homologues of benzene, a hydroxyl group may be introduced into a fatty lateral chain, and in such a case the resulting acid is an alcohol acid; such an acid is mandelic acid

$$C_6H_5{\cdot}CH(OH)COOH$$

I. **Monohydroxyaromatic acids.** The most important members of this group of acids are salicylic, *m*- and *p*-hydroxybenzoic and anisic acids (*q.v.*). They occur in nature; thus salicylic acid is found in the buds of *Spiræa Ulmaria* (Linn.) and as the methyl ester in oil of winter-green.

General methods of preparation.

(i) By the action of nitrous acid on the amino-acids, *e.g.* salicylic acid from anthranilic acid.

(ii) By fusing the sulphonic acids with alkalis, *e.g.* salicylic acid from *o*-toluenesulphonic acid.

(iii) By fusing the homologous phenols with alkalis, when the methyl group attached to the benzene nucleus will be oxidised to the carboxyl group, *e.g.* salicylic acid from *p*-cresol.

(iv) By fusing the phenol aldehydes with potash, *e.g.* salicylic acid from salicylaldehyde.

(v) By the action of carbon dioxide on the dry sodium salts of the phenols at high temperatures when the carbonic acid usually enters the ring in the position ortho to the hydroxyl group, *e.g.* salicylic acid from sodium phenate.

(vi) By boiling the phenols with carbon tetrachloride and caustic potash, the carboxyl group entering the ring generally in a position para to the hydroxyl groups: o-acids are formed in small amounts, *e.g.* *p*-hydroxybenzoic acid from phenol, carbon tetrachloride, and caustic potash.

Properties.—When these acids react with carbonates only the hydrogen of the carboxyl group is replaced by metal; but with alkaline hydroxides they behave like feeble dibasic acids, and the hydrogen of the phenolic hydroxyl is also replaced: *e.g.* in disodium salicylate $C_6H_4(ONa)COONa$. Carbon dioxide will convert the latter into the former. The *o*-acids, unlike the *m*- and *p*-acids, volatilise in aqueous vapour, are coloured violet by ferric chloride and dissolve in chloroform. The *m*-acids are coloured red brown when heated with concentrated sulphuric acid and are converted into hydroxyanthraquinones: they are usually more stable than the *o*- and *p* acids. Boiling hydrochloric acid decomposes the *p*-acids into carbon dioxide and phenols. All the hydroxy acids decompose into phenol and carbon dioxide when distilled with lime.

II. **Dihydroxyaromatic acids.** The most important member of this class is protocatechuic acid (*q.v.*). These acids may be prepared by the same methods as were used for the monohydroxy acids (*v. supra*). The carboxyl group is more readily introduced into the dihydroxybenzenes than into the monohydroxybenzenes. This may be effected by heating the compounds with a solution of ammonium or sodium carbonate at 100°-130°. The dihydroxybenzoic acids break down when heated, into carbon dioxide and dihydroxybenzenes.

III. **Trihydroxyaromatic acids.** The most important members of this group are gallic and tannic acids (*q.v.*).

HYDROXYANTHRAQUINONE *v.* ALIZARIN AND ALLIED COLOURING MATTERS.

HYDROXYBENZALDEHYDE *v.* SALICYLALDEHYDE.

HYDROXYBENZENES *v.* PHENOL AND ITS HOMOLOGUES.

HYDROXYBUTYRIC ACIDS $C_4H_8O_3$.

α-Hydroxybutyric acid

$$CH_3{\cdot}CH_2{\cdot}CH(OH)CO_2H$$

Prepared by treating α-chloro- or α-bromobutyric acid with baryta (Markownikow, Annalen, 153, 242) or with moist silver oxide (Naumann, Annalen, 119, 115; Friedel and Machuca, *ibid.* 120, 279); by treating the cyanhydrin of propionaldehyde with hydrochloric acid and saponifying the nitrile thus produced (Prbzibyck, J. Russ. Chem. Soc. 8, 335); by heating ethyltartronic acid at 180° (Guthzeit, Annalen, 209, 234); by boiling 100 grams of α-bromobutyric acid, 500 c.c. of water and 1 molecular proportion of potassium carbonate for 5 to 6 hours (Bischoff and Walden, *ibid.* 279, 104). Forms white crystals, m.p. 43°–44°, sublimes at 60°–70° and boils at 225°. Chromic acid oxidises it to acetic and propionic acids, whilst electrolysis of a concentrated solution of the sodium salt results in the production of propionaldehyde and formic acid (Miller and Hofer, Ber. 1894, 468). It has been resolved into its optically active components by fractional crystallisation of the brucine salts (Guye and Jordan, Compt. rend. 120, 562, 632, 1274).

β-Hydroxybutyric acid

$$CH_3{\cdot}CH(OH)CH_2{\cdot}CO_2H$$

Prepared by the reduction of aceto-acetic ester with sodium amalgam (Wislicenus, Annalen, 149, 205); by the action of potassium cyanide on α-propylenechlorhydrin and saponification of the nitrile thus formed (Markownikow, *ibid.* 153, 237). It forms a thick syrup, which is volatile in steam and on heating decomposes into water and crotonic acid. It has been resolved into its optically active components by fractional crystallisation of the quinine salts (McKenzie, Chem. Soc. Trans. 1902, 1402). *l*-β-Hydroxybutyric acid occurs in the urine in considerable quantities in cases of *diabetes mellitus* (Laud, Chem. Zentr. 1899, ii. 63; Bergell, Zeitsch. physiol. Chem. 1901, 33, 310; Minkowski, Chem. Soc. Abstr. 1885, 413; Kulz, Zeitsch. Biol. 20, 165). (For estimation in urine *v.* Schaffer, J. Biol. Chem. 1908, 5, 211; Black, *ibid.* 207.) The liver cells contain an enzyme, ***β-hydroxybutyrase***, which converts β-hydroxybutyric acid into aceto-acetic acid (Wakeman and Dakin, *ibid.* 1909, 6, 373).

γ-Hydroxybutyric acid

$$CH_2(OH)CH_2{\cdot}CH_2{\cdot}CO_2H$$

readily loses water even at the ordinary temperature passing into the cyclic ester, butyrolactone $\overline{CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}O}$. Butyrolactone was discovered by Saytzeff in 1873, but he regarded it as the dialdehyde of succinic acid. He prepared it by the reduction of succinyl chloride in acetic acid with sodium amalgam (Annalen, 171, 261) It may also be prepared by the distillation of γ-chlorobutyric acid at 180°–200° (Henry, Bull. Soc. chim. [ii.] 45, 341); by the interaction of ethylene chlorhydrin and acetoacetic ester and decomposing the resulting product with baryta (Chanlaroff, Annalen, 226, 325); by treating a solution of succinic anhydride in ether with sodium amalgam and gradually adding hydrochloric acid to the product (Fichter and Herbrand, Ber. 1896, 1192); by heating γ-phenoxybutyric acid with fuming hydrobromic acid (Bentley, Haworth and Perkin, Chem. Soc. Trans. 1896, 168); by the reduction of aldehydopropionic acid with sodium amalgam (Perkin and Sprankling, *ibid.* 1899, 17). It is a colourless oil, b.p. 206° (Fittig and Roeder, Annalen, 227, 22); sp.gr. 1·1286 15°/0°; it is volatile in steam. Chromic acid oxidises it to succinic acid; heating with hydriodic acid converts it into iodobutyric acid (Saytzeff, J. pr. Chem. 25, [ii.] 70). It reacts with magnesium methyl iodide, forming δ-methylpentane-αδ-diol (Henry, Compt. rend. 1906, 143, 1221).

α-Hydroxyisobutyric acid (*Butyl-lactinic acid, Acetonic acid, Dimethyl oxalic acid*)

$$(CH_3)_2C(OH){\cdot}CO_2H$$

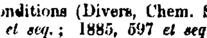
Prepared by treating acetone with prussic and hydrochloric acids (Staedeler, Annalen, 111, 320; Markownikow, *ibid.* 146, 339); by treating dimethyloxalic ester with zinc and methyl iodide (Frankland and Duppa, *ibid.* 135, 25); by heating acetonechloroform to 180° with water or by boiling with caustic soda (Willgerodt and Schiff, J. pr. Chem. 41, [ii.] 519; Ber. 1882, 2307); by heating α-bromo- or α-chloro*iso*butyric acid with water to 180°, with baryta, or with caustic soda (Markownikow, Annalen, 153, 228; Fittig, *ibid.* 200, 70; Ostropjatow, J. Russ. Phys. Chem. Soc. 28, 51); by treating α-amino*iso*butyric acid with sodium nitrite (Tiemann and Friedländer, Ber. 1881, 1973); by treating *iso*butyric acid with potassium permanganate (Meyer, Annalen, 219, 240). It forms hygroscopic prisms which sublime at about 50°, and when freshly sublimed melt at 79°; b.p. 212°; volatile in steam. Oxidation with chromic acid converts it into acetic acid, acetone, and carbon dioxide; fusion with caustic soda yields acetone; beating with phosphorus pentoxide yields acetaldehyde, acetone, acetic acid, and other products (Bischoff and Walden, Annalen, 279, 111). *Acetone chloroform* (*q.v.*)

$$(CH_3)_2C(OH)CCl_3$$

is an interesting derivative of this acid.

HYDROXYCODEINE *v.* OPIUM.

HYDROXYETHYLANILINE



Prepared by heating a mixture of aniline, water, and ethyleuechlorhydrin. B.p. 286°, sp.gr. 1·11 at 0°, slightly soluble in water; readily soluble in alcohol and ether. Used in the manufacture of indigo.

HYDROXYLAMINE NH_2OH. Discovered by Lossen (Annalen, Suppl. 1868, 6, 220) in 1865, but until 1891 only known in the form of salts or in aqueous solution. Obtained by the reduction of nitric acid with metals under suitable conditions (Divers, Chem. Soc. Trans. 1883, 443 *et seq.*; 1885, 597 *et seq.*); by the reduction of nitrates, nitro bodies, &c., with finely divided metals (Wohl, Eng. Pat. 11216; J. Soc. Chem. Ind. 1895, 595); by the electrolytic reduction of nitric acid, nitrous acid, or their salts or other derivatives in the presence of a second acid electrolyte at a low temperature (Boehringer and Söhne, D. R. PP. [illegible], 137697; Fr. Pat. 319187; J. Soc. Chem. Ind. 1902, 1458; Compagnie Parisienne de Couleurs d'Aniline, Fr. Pat. 322943; J. Soc. Chem. Ind. 1903, 425; Tafel, Zeitsch. anorg. Chem. 1902, 31, 289; Schoch and Pritchett, J. Amer. Chem. Soc. 1916, 38, 2042); by the reduction of nitrites with sodium amalgam (Divers, Chem. Soc. Trans. 1899, 89) or with sulphites (Raschig, Eng. Pat. 3028; J. Soc. Chem. Ind. 1888, 210; Eichkoff, Arch. Pharm. 27, [iii.] 713; Lidoff, J. Russ. Chem. Soc. 1884, 751; Divers and Haga, Chem. Soc. Trans. 1887, 661; 1896, 1665). It is best prepared by taking a concentrated aqueous solution of commercial sodium nitrite (2 mols.) and sodium carbonate (1 mol.) and passing in sulphur dioxide at −2° to −3° with constant stirring until it is just acid. The solution is warmed gently with a few drops of sulphuric acid and then kept at 90°–95° for two days. It is then neutralised with sodium carbonate, evaporated until the solution weighs about 10½–11 times as much as the sodium nitrite originally taken, when on cooling nearly all the sodium sulphate crystallises out. The hydroxylamine sulphate is obtained from the mother liquors and purified by recrystallisation (Divers and Haga, *l.c.*). Jouve (Compt. rend. 128, 434) has prepared hydroxylamine synthetically by the direct union of hydrogen and nitric acid in the presence of spongy platinum at 115°–120°. The anhydrous compound may be obtained by dissolving hydroxylamine hydrochloride in absolute methyl alcohol, adding a solution of sodium methoxide in the same solvent, separating the sodium chloride so formed and distilling off the greater part of the methyl alcohol under 100 mm. pressure. The residue is distilled in small portions under 20 mm. pressure with the addition of a little vaseline to prevent frothing. When the solid hydroxylamine begins to come over, the receiver is changed and cooled to 0°, care being taken that the hydroxylamine vapour does not come in contact with air at 60°–70°, as then explosions occur (Lobry de Bruyn, Rec. trav. chim. 10, 100; 11, 18; *v.* also Bruhl, Ber. 1894, 1347). Crismer (Bull. Soc. chim. 6, [iii.] 793) obtains it by heating zinc dihydroxylamine chloride, and Uhlenhuth (Annalen, 311, 117) by the distillation of the phosphate under reduced pressure; the solid thus obtained may be purified by crystallisation from absolute alcohol at −18° (Ebler and Schott, J. pr. Chem. 1908, 78, [ii.] 289).

According to Baudisch and Jenner (Ber. 1916, 49, 1182) hydroxylamine may be obtained by cautiously adding the finely powdered dry sulphate to liquid ammonia in a quartz tube, removing the ammonia by evacuation, and extracting the free hydroxylamine by alcohol.

Hydroxylamine forms white inodorous scales or hard needles, sp.gr. 1·3 (*circa*), m.p. 33·05°, b.p. 58° under 22 mm. Heated to 100° it decomposes, ammonia, nitrous and hyponitrous acids being the first products of decomposition and these then interact with the formation of nitrogen and nitrous oxide. Readily soluble in water, and to a less extent in ethyl and methyl alcohols, and in boiling ether (De Bruyn, Ber. 1894, 967). When pure it is stable below 15°, but alkali decomposes it. The aqueous solution is colourless and odourless, has a strong alkaline reaction, and gives precipitates, insoluble in excess, with salts of Zn, Ni, Fe, Al, Cr, but not with those of the alkaline earths. In its general reactions resembles a solution of ammonia, although it is less basic than that substance. It acts as a strong reducing agent, *e.g.* with $CuSO_4$ solution it gives a red precipitate of Cu_2O; it reduces $HgCl_2$ to HgCl, and precipitates the metals from solutions of $AgNO_3$, $AuCl_3$, and $PtCl_4$. It can also act as an oxidising agent being itself reduced to ammonia (Haber, Ber. 1896, 2444; Biltz, *ibid.* 1896, 2080; Dunstan and Dymond, Chem. Soc. Trans. 1887, 646). Thus in alkaline solution it converts ferrous hydroxide into ferric hydroxide, whilst in acid solution it reduces ferric chloride to ferrous chloride. Oxidation converts hydroxylamine into nitrous oxide and nitric oxide (Arndt, Ber. 1900, 33) and caustic soda decomposes it into nitrogen, nitrous oxide, nitrous acid and water (Kolotoff, J. Russ. Phys. Chem. Soc. 25, 295).

The salts of hydroxylamine are readily soluble in water and alcohol; they crystallise well and are anhydrous.

By treating hydroxylamine sulphate in the cold with sodium nitrite and then adding silver nitrate, a yellow precipitate of silver hyponitrite is obtained (Wislicenus, Ber. 1893, 771; Tanatar, J. Russ. Phys. Chem. Soc. 25, 342; Ber. 1894, 187). By passing sulphur dioxide through a solution of the hydrochloride or sulphate, ammonium sulphate is produced (Tanatar, Ber. 1899, 241, 1016). Elber and Schott (J. pr. Chem. 1908, ii. 78, 289) have prepared metallic salts of the type $R(ONH_2)_2$, where R is any divalent metal: alkyl hydroxylamines have been prepared by the action of alkyl halides on hydroxylamine (Dunstan and Goulding, Chem. Soc. Trans. 1899, 792; *v.* also *ibid.* 1896, 839; De Bruyn, Rec. trav. chim. 15, 185).

Detection and estimation.—Hydroxylamine may be detected by its action in reducing Barreswil's solution with the formation of cuprous oxide (Adams and Overman, J. Amer. Chem. Soc. 31, 637); by adding sodium nitroprusside to a neutral solution and then a little caustic sode, when a magenta red coloration is produced (Angeli, Gazz. chim. ital. 23, ii. 102); or by treating it with sodium acetate and benzoyl chloride with the formation of benzhydroxamic acid which gives a violet-red coloration with ferric chloride (Bamberger, Ber. 1899, 1805). It may be estimated by titration in alkaline solution with mercury acetamide, which is reduced to metallic mercury (Forster, Chem. Soc. Trans. 1898, 785); by oxidation with vanadic sulphate, measuring the nitrogen evolved and titrating the vanadous sulphate with potassium permanganate (Hofmann and Küspert, Ber. 1896, 64); by adding excess of standard titanium trichloride and titrating back the excess with potassium permanganate (Stähler, *ibid.* 1904, 4732; *v.* also *ibid.* 1909, 2695); by titrating the solution with potassium permanganate after the addition of sodium oxalate (Simon, Compt. rend 135, 1339); by reducing ferric sulphate and titrating the ferrous salt by permanganate (Raschig); by boiling with excess of N/10 silver nitrate solution, ammonia, and caustic soda and estimating the silver nitrate unacted upon (Denigés, Ann. Chim. Phys. 7, [vi.] 427). Jones and Carpenter (Chem. Soc. Trans. 1903, 1394) add the solution containing the hydroxylamine to a hot solution of potassium copper carbonate or tartrate with stirring. The solution is boiled, filtered, the precipitate washed with hot water and dissolved in ferrous sulphate in an atmosphere of carbon dioxide. The ferrous salt is titrated back with potassium permanganate.

$$4 \text{ mols. } K_2Mn_2O_8 = 10 \text{ mols. } NH_2OH$$

Rupp and Mäder describe volumetric processes depending on the oxidising action of bromine (Arch. der Pharm. 1913, 251, 295; Analyst, 1913, 437).

Bray, Simpson, and Mackenzie (J. Amer. Chem. Soc. 1919, 41, 1363) have investigated three methods for the estimation of hydroxylamine: (1) reduction to ammonia by excess of titanous salt in acid solution; (2) oxidation to nitrous oxide by excess ferric sulphate in sulphuric acid solution, with titration of the ferrous salt by permanganate solution; and (3) oxidation to nitrous oxide by iodine in a solution kept neutral by means of disodium hydrogen phosphate. The titanous salt and ferric salt methods were found to be accurate, but the iodine method was unsatisfactory.

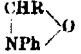
Schaeffer (Bull. Mulhouse, 1883) has applied the reducing properties of hydroxylamine in order to discharge manganese brown. The hydrochloride NH_2OH,HCl must be used. On printing this upon a manganese ground the latter is instantly reduced to manganese chloride. A very dark indigo, blue-dyed on manganese, is lowered to a lighter and brighter blue by the elimination of the MnO_2. In like manner nankin, chamois, and similar colours can be discharged white (J. Soc. Chem. Ind. 3, 166).

Hydroxylamine and its salts have been used as developers in photography, and for recovering silver from fixing bath solutions and waste liquors (Lainer, J. Soc. Chem. Ind. 1890, 890). It is a powerful antiseptic (Marpmann, Pharm. Centr. N.F. 10, 245) and has been used as a substitute for chrysarobin and pyrogallic acid, as it does not discolour the skin or bandages and has a strong reducing action (Schwarz, Pharm. Zeit. 33, 659).

Ethylhydroxylamines *v.* ETHYL.

β-Phenylhydroxylamine C_6H_5NHOH. Prepared by the reduction of nitrobenzene (1) in water with zinc (Bamberger, Ber. 1894, 27, 1348, 1548; Wohl, *ibid.* 1432); (2) in alcohol with zinc (Wohl, *ibid.* 1434; D. R. P. 84138; Frdl. iv. 44), or the zinc-copper couple (Wohl, D. R. P. 84891; *ibid.* 46) in the presence of anhydrous calcium chloride; (3) in aqueous alcohol with zinc amalgam in the presence of aluminium sulphate (Bamberger and Knecht, Ber. 1896, 29, 864); (4) in ether with zinc in the presence of anhydrous calcium chloride (Goldschmidt, *ibid.* 2307); (5) in aqueous ether with aluminium amalgam (Wislicenus, *ibid.* 494; J. pr. Chem. [ii.] 54, 57); (6) in ammonium chloride with zinc (Kalle & Co. D. R. P. 89978; Frdl. iv. 47); (7) electrolytically in acetic acid (Haber, Zeitsch. Elektrochem. 1898, 5, 77) or in alcoholic ammonia (Schmidt, Zeitsch. physikal. Chem. 32, 272); by the oxidation of aniline in ethereal solution with Caro's acid (Bamberger and Tschirner, Ber. 1899, 32, 343).

Baudisch (Chem. Zeit. 1911, 35, 913) gives the following details for the preparation of phenylhydroxylamine with a view to its conversion to 'cupferron' (*q.v.*). Sixty grams of nitrobenzene, 1000 c.c. of water, and 30 grams of ammonium chloride are well stirred, and to the white emulsion is added 80 grams of zinc dust in very small quantities, so that the temperature keeps between 16° and 18°. When the odour of nitrobenzene has completely disappeared, the solution is drawn off from the zinc hydroxide, and after cooling to 0° by means of ice, the liquid is saturated with salt, which causes an abundant crystalline precipitate of phenylhydroxylamine. Great care must be taken not to let this substance come in contact with the skin, as it is very poisonous (Chem. Soc. Abtr. 1911, ii. 939). For further details, *see* Marvel and Kamm, J. Amer. Chem. Soc. 1919, 41, 276; Analyst, 1919, 142. The yield depends on the quality of the zinc dust, but consistently good yields may be obtained by previously treating the zinc dust with 2 p.c. mercurous nitrate solution slightly acidified with nitric acid (Kasanof, J. Ind. Eng. Chem. 1920, 12, 799).

β-Phenylhydroxylamine forms colourless needles, m.p. 81°–82°; soluble in 10 parts of hot and 50 of cold water, readily soluble in alcohol, ether, carbon disulphide, and chloroform, sparingly so in petroleum. It dissolves in sulphuric acid with a deep blue colour. By heating at 100° azobenzene together with aniline, azoxybenzene, and other products are formed. Oxidation with potassium permanganate gives first nitrosobenzene, then nitrogen and azoxybenzene (Bamberger and Tschirner, Ber. 1899, 32, 342); in dilute neutral solution hydrogen peroxide yields azoxybenzene, in alkaline solution azoxybenzene and nitrobenzene (Bamberger, *ibid.* 1900, 33, 119). In the presence of hydroxylamine and air it is partly oxidised to azoxybenzene and partly reduced to aniline, phenylazoimide, and benzeneazohydroxyamide also being formed (Bamberger, *ibid.* 1902, 35, 3893). It dissolves in sodium hydroxide forming a sodium salt which in the absence of air yields azoxybenzene, and in the presence of air azoxybenzene and nitrobenzene; alcoholic potash yields azobenzene (Bamberger and Brady, *ibid.* 1900, 33, 271). Mineral acids yield *p*-aminophenol and azoxybenzene; alcoholic sulphuric acid gives azoxybenzene, *o*- and *p*-phenetidine, *o*- and *p*-aminophenols, aniline and other compounds (Bamberger and Lagutt, *ibid.* 1898, 31, 1501). With aromatic aldehydes it yields phenylaldoximes of the type  $\begin{array}{l}CHR\\ |\\ NPh\end{array}\!\!>O$ (Plancher and Piccinini, Atti. R. Accad. Lincei. 1905, [v.] 14, ii. 36). (For constitution, *v.* Bruhl, Zeitsch. physikal. Chem. 1898, 26, 47.)

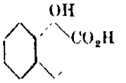
Nitrosophenylhydroxylamine $C_6H_5N(NO)OH$. Prepared by the action of sodium nitrite and dilute sulphuric acid on β-phenylhydroxylamine (Wohl, Ber. 1894, 27, 1435; Bamberger, *ibid.* 1553); or by the interaction of hydroxylamine and nitrobenzene in alcoholic solution in the presence of sodium ethoxide (Angeli, *ibid.* 1896, 29, 1885; Angelico, Atti. R. Accad. Lincei, [v.] 8, ii. 28).

It crystallises from petroleum in colourless needles, melting at 58°–59° and decomposing at 75°; sparingly soluble in water, readily so in most organic solvents. On heating it decomposes into nitrosobenzene and other substances (Bamberger, Ber. 1898, 31, 574, 1507). Alcoholic or ethereal solutions give a brownish-red coloration with a few drops of dilute ferric chloride (Bamberger and Ekecrantz, *ibid.* 1896, 29, 2412). Reduction with sodium amalgam yields phenylhydrazine; oxidation with potassium permanganate or sodium hypochlorite, nitrosobenzene. By heating with dilute mineral acids nitrosobenzene is formed, whilst nitrous acid yields benzenediazonium nitrite.

Cupferron, *Ammonium nitrosophenylhydroxylamine*, $C_6H_5(NO)N{\cdot}ONH_4$ is prepared by dissolving β-phenylhydroxylamine in ether at 0°, passing in dry ammonia and adding excess of amyl nitrite, when a snow-white crystalline mass of ammonium nitrosophenylhydroxylamine is formed (Baudisch and King, J. Ind. Eng. Chem. 1911, 3, 629; Marvel and Kamm, J. Amer. Chem. Soc. 1919, 41, 276; Analyst, 1919, 142).

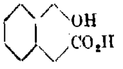
Cupferron is used in quantitative analysis for separating copper and iron from most of the metals. The iron and copper are precipitated in strongly acid solution with cupferron, the precipitate filtered, washed with water, and finally with ammonium hydroxide. The latter dissolves the copper, but not the ferric salt. The ferric salt is soluble in chloroform, ether, acetone, &c., and may be dissolved and separated from other salts, such as those of lead, silver, or tin, which may have been precipitated with it (Baudisch, Chem. Zeit. 1909, 33, 1298; 1911, 35, 913; Biltz and Hödtke, Zeitsch. anorg. Chem. 1910, 66, 426; Hanus and Soukup, *ibid.* 68, 52; Fresenius, Zeitsch. anal. Chem. 1911, 50, 35). It precipitates titanium as a bright yellow salt $[C_6H_5(NO)NO]_4Ti$, which on ignition yields TiO_2. This reagent may be used to separate titanium from aluminium, chromium, nickel, cobalt, and manganese (Bellucci and Grassi, Gazz. chim. ital. 1913, 43, 570), or for the quantitative separation of zirconium, titanium, iron, manganese, and aluminium, or in the analysis of zircon and baddeleyite (Brown, J. Amer. Chem. Soc. 1917, 39, 2358). The reagent can be used for the accurate estimation of iron, copper, titanium, zirconium, thorium, and vanadium; the presence of other metals may interfere. Hence the cupferron method is only applicable when the qualitative composition of the material is known (Lundell and Knowles, J. Ind. Eng. Chem. 1920, 12, 344). For a bibliography of cupferron and its applications in analysis, *see* Analyst, 1920, 58.

HYDROXY-2-NAPHTHOIC ACID



Obtained by the action of carbon dioxide on sodium-α-naphthoxide at 120°–145° under pressure. The product dissolved in water is treated with hydrochloric acid and recrystallised. Needles, m.p. 187°.

2 Hydroxy-3-Naphthoic acid



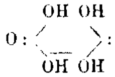
Prepared by acting on sodium-β-naphthoxide by carbon dioxide at 200°–250° under pressure and treating the product dissolved in water with hydrochloric acid. Yellow scales, m.p. 216°.

p-HYDROXYPHENYLETHYLAMINE *v.* Ergot.

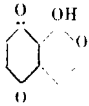
HYDROXYQUINOL *v.* Phenol and its homologues.

HYDROXYQUINOLINE *v.* Quinoline.

HYDROXYQUINONE COLOURING MATTERS. The hydroxyquinones form an important group of mordant colouring matters which are characterised by containing at least one hydroxyl group adjacent (ortho- or peri-) to an oxygen atom of a quinone, but usually two hydroxyl groups in the ortho- position with respect to one another. They possess the property of forming insoluble, coloured salts with certain metallic oxides, and therefore, when dyed on a fabric impregnated (mordanted) with such oxides, for example, the oxides of aluminium, chromium, and iron, lakes are formed which are extremely fast. The simplest compound possessing the above requirements is tetrahydroxy-*p*-benzoquinone

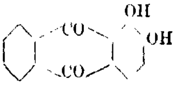


but its dyeing properties are not sufficiently intense for it to be of practical value. This desideratum is first reached in the naphthalene series in the case of dihydroxynaphthaquinone or



Naphthazarin, which comes on the market in the form of its sodium bisulphite compound, Alizarin black (*see* under Naphthalene).

By far the most valuable and important hydroxyquinones are those belonging to the anthracene series, of which a large number are manufactured. The simplest and best known of these is dihydroxyanthraquinone or alizarin



(*See* Alizarin colouring matters.) J. C. C.

HYDROXYSTEARIC ACIDS $C_{18}H_{36}O_3$.

α-Hydroxystearic acid

$$CH_3[CH_2]_{15}CH(OH)CO_2H$$

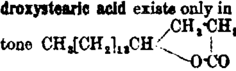
Prepared by treating α-bromostearic acid with aqueous potash. Separates from a mixture of benzene and petroleum as a crystalline powder, m.p. 91°–92° (Hell and Sadomsky, Ber. 1891, 2391; Le Sueur, Chem. Soc. Trans. 1904, 827). By heating it to 270°, it yields margaric aldehyde $C_{16}H_{33}{\cdot}CHO$, a lactide $C_{36}H_{68}O_4$, formic acid, water and carbon dioxide.

β-Hydroxystearic acid

$$CH_3[CH_2]_{14}CH(OH)CH_2{\cdot}CO_2H$$

Prepared by treating β-bromostearic acid with aqueous potash. Crystallises from chloroform in white plates, m.p. 89° (Ponzio, Atti. R. Accad. Sci. Torino, 1905, 40, 970).

γ-Hydroxystearic acid exists only in the form of a lactone



$$CH_3[CH_2]_{13}CH\begin{array}{l}\diagup CH_2{\cdot}CH_2\\ \qquad\quad |\\ \diagdown O{\cdot}CO\end{array}$$

Obtained by treating the anhydride of γ-hydroxyoleic acid with potash (Geitel, J. pr. Chem. 37, [ii.] 85). Prepared by heating oleic acid with anhydrous zinc chloride. Oxidation with chromic acid in glacial acetic acid converts it liquid monobasic and small quantities of di-p acids, including succinic acid and γ-keto-ic acid $CH_3[CH_2]_{13}CO[CH_2]_2CO_2H$, m.p. (Shukoff and Schestakoff, J. Russ. Phys. m. Soc. 1903, 35, 1).

-Hydroxystearic acid

$$CH_3[CH_2]_7{\cdot}CH(OH)[CH_2]_8CO_2H$$

acid was formerly described as *β-hydrox-* *ric acid* (A. C. and M. Saytzew, J. Russ. Phys. m. Soc. 1886, 328; 17, 426; J. pr. Chem. [ii.] 369, 384; Fremy, Annalen, 19, 296; 20, 33, 10; Ann. Chim. Phys. 65, [ii.] 113; anejew, J. Russ. Phys. Chem. Soc. 18, 41; tel, J. pr. Chem. 37, [ii.] 81; Leichti and ia, Ber. 1883, 2458). Shukoff and Schestakoff (J. Russ. Phys. Chem. Soc. 1903, 35, 1) have shown that its constitution is that of -hydroxystearic acid. It is prepared from the sulpho or iodo derivative of oleic acid, or best by the action of sulphuric acid on oleic acid; m.p. 83°–85°. It may also be obtained from elaidic acid by the action of sulphuric acid and subsequent treatment with alcoholic potash (Tscherbakow and Saytzew, J. pr. Chem. 57, [ii.] 27). By heating to 100° it yields an anhydride; oxidation with chromic acid in glacial acetic acid converts it into sebacic, azelaic, and traces of suberic and liquid monobasic acids and ι-keto-stearic acid $CH_3[CH_2]_7CO[CH_2]_7CO_2H$, m.p. 76°. Molinari and Barosi (Ber. 1908, 2794) have obtained an acid by the decomposition of the ozonide of oleic acid and consider it to be formed by the aldol condensation of nonaldehyde with nonoic acid, and hence they consider it to be ι-hydroxystearic acid; it melts at 41°, and hence is either impure or a hydroxystearic acid containing the hydroxyl group in some other position.

κ-Hydroxystearic acid

$$CH_3[CH_2]_6CH(OH)[CH_2]_9CO_2H$$

This acid was formerly described as *a-hydroxystearic acid* (Saytzew, J. pr. Chem. 37, [ii.] 277, 284). Shukoff and Schestakoff (J. Russ. Phys. Chem. Soc. 1903, 35, 1) have shown that its constitution is that of κ-hydroxystearic acid; m.p. 84°–85°. Prepared by the action of sulphuric acid on *iso*oleic acid. Oxidation with chromic acid in glacial acetic acid yields sebacic acid, nonylene-*aι*-dicarboxylic acid (m.p. 124°), and κ-ketostearic acid,

$$CH_3[CH_2]_6CO[CH_2]_9CO_2H$$

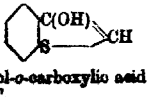
m.p. 65°.

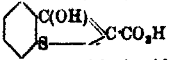
λ-Hydroxystearic acid (12-*Hydroxystearic acid*)

$$CH_3[CH_2]_5CH(OH)[CH_2]_{10}CO_2H$$

Prepared from the methyl ester which is obtained by the reduction of the methyl ester of ricinoleic acid; m.p. 78° (Grün and Woldenberg, J. Amer. Chem. Soc. 1909, 31, 490). Kasansky (J. Russ. Phys. Chem. Soc. 1900, 32, 149), by acetylating ricinoleic acid, followed by bromination and reduction, obtained a hydroxystearic acid (m.p. 81°–82°) which is possibly identical with the above.

HYDROXYTHIONAPHTHEN (*thioindoxyl*)



Phenylthioglycol-o-carboxylic acid is introduced into an aqueous solution of caustic soda, and heated to 170°–200°. The product is treated with water and the *2-hydroxythionapthen-1-carboxylic acid*  is precipitated by the addition of hydrochloric acid. By heating the acidified solution so long as carbon dioxide is evolved 2-hydroxythionaphthen is produced and separates out on cooling (Kalle & Co. D. R. P. 192075). Acetic anhydride may also be used to convert the phenylthioglycol-o-carboxylic acid in hydroxythionaphthen (*idem*, D. R. P. 198712), or the acid may be heated alone at 230° so long as gas is evolved (*idem*, D. R. PP. 188702, 198713) or with paraffin, glycerol (with or without sulphuric acid), or aniline. In the last case the aniline compound is boiled with a dilute acid when 2-hydroxythionaphthen distils with steam and forms white needles (*idem*, D. R. P. 202351). May also be formed by condensing chloroacetic acid with *o*-aminothiophenol and converting the *o*-aminophenylthioglycol-*o*-carboxylic acid in the cyano-compound by diazotising and boiling with dilute sodium hydroxide solution: the 2-aminothionaphthen-1-carboxylic acid is transformed into 2-hydroxythionaphthen by boiling with dilute acid (Kalle & Co. D. R. P. 184496), or more directly by converting the cyano-derivative by treating with sulphuric acid (*idem*, D. R. P. 190291) or caustic soda solution (*idem*, D. R. P. 190674).

Esters and alkali salts of methylthiosalicylic acid may also be transformed into 2-hydroxythionaphthen (Farbw. vorm. Meister, Lucius and Bruning, D. R. PP 200200, 200428, 200593).

Thiosalicylic acid treated with dichlorethylene (acetylene dichloride) CHCl : CHCl yields acetylene-*bis*thiosalicylic acid,

$$CO_2H{\cdot}C_6H_4{\cdot}S{\cdot}CH{\cdot}CH{\cdot}S{\cdot}C_6H_4{\cdot}CO_2H$$

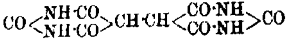
which when heated with a mixture of caustic potash and soda at 220°–230°, dissolved in water, acidified, and steam-distilled, yields 2-hydroxythionaphthen (Bad. Anilin and Soda Fabrik, D. R. P. 221465). M.p. 71°. Used in the manufacture of thioindigo dyes.

HYDROXYTHIONAPHTHEN-1-CARBOXYLIC ACID (*thioindoxyl carboxylic acid*). Melts at 213°. Sparingly soluble in water, benzene, or light petroleum; more soluble in alcohol, acetone, or ethyl acetate. For preparation, *see* foregoing article.

HYDROZINCITE. Hydrated basic carbonate of zinc, $ZnCO_3{\cdot}2Zn(OH)_2$, containing Zn 60·5 p.c., of common occurrence as an alteration product of other ores of zinc. It is found in the upper levels of most zinc mines as soft, snow-white encrustrations often in stalactitic, botryoidal, or other forms. Large masses with an earthy or chalky texture are not uncommon; sp.gr. 3·6–3·8 Much of the material often regarded as smithsonite ($ZnCO_3$) is really hydrozincite, as shown by its lower degree of hardness (H. 2–2½, that of smithsonite being 5) and the presence of water. Large quantities have been obtained from the zinc mines of province Santander in Spain, Bleiberg in Carinthia, Sardinia, &c. It has been observed as a mineral of recent formation in the old galleries of lead-zinc mines in North Wales.

L. J. S

HYDURILIC ACID $C_8H_6O_6N_4,H_2O$ or $2H_2O$;

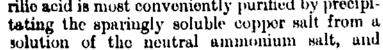


$$\mathrm{CO}<\begin{matrix}\mathrm{NH\cdot CO}\\\mathrm{NH\cdot CO}\end{matrix}>\mathrm{CH\cdot CH}<\begin{matrix}\mathrm{CO\cdot NH}\\\mathrm{CO\cdot NH}\end{matrix}>\mathrm{CO}$$

was first prepared by Schlieper (Annalen, 1845, 56, 11), who obtained the acid **ammonium** salt together with alloxan by the action of nitric acid (sp.gr. 1·25) on uric acid. It is also prepared (2) in the form of its ammonium salt by prolonged boiling of alloxan or alloxantin with very dilute sulphuric acid (Finch, Annalen, 1864, 132, 303); (3) by heating crystallised alloxantin in a tube at 170° when it is converted quantitatively into hydurilic acid, according to the equation

$$2C_8H_4O_7N_4+3H_2O$$
$$=C_8H_6O_6N_4+4NH_3+(COOH)_2+2CO+4CO_2$$

or alloxan is similarly decomposed (Murdoch and Doebner, Ber. 1876, 9, 1102); (4) in the form of its acid ammonium salt by heating dialuric acid with glycerol at 150°, formic acid and carbon dioxide being formed at the same time (Baeyer, Annalen, 1863, 127, 14; *cf.* Biltz and Heyn, Ber. 1919, 52 [B] 1298); (5) together with glycine and carbon dioxide by heating uric acid with twice its weight of concentrated sulphuric acid (Schultzen and Filehne, Ber. 1868, 1, 150), by oxidation of barbituric acid in aqueous solution with potassium permanganate (Biltz and Heyn, *l.c.*); (6) by reducing dibromobarbituric acid with hydrogen iodide (Baeyer, Annalen, 1864, 130, 133); and it is also formed to a small extent by reducing alloxantin with sulphuretted hydrogen (Murdoch and Doebner, *l.c.*); (7) by the condensation of ethyl ethanetetracarboxylate with carbamide in the presence of sodium ethoxide at 60°–70°, or by the hydrolysis of ethanetetracarbonylguanide

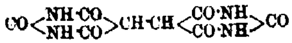


$$\mathrm{NH{:}C}<\begin{matrix}\mathrm{NH\cdot CO}\\\mathrm{NH\cdot CO}\end{matrix}>\mathrm{CH\cdot CH}<\begin{matrix}\mathrm{CO\cdot NH}\\\mathrm{CO\cdot NH}\end{matrix}>\mathrm{C{:}NH},H_2O$$

by means of dilute hydrochloric acid at 150° (Conrad, Annalen, 1907, 365, 24; *cf.* Roeder, Ber. 1913, 46, 2560): whereas ethyl ethanetetracarboxylate and carbamide yield only a trace of hydurilic acid, *dithiohydurilic* acid is readily obtained from the ester and thiocarbamide; this compound remains unaltered at 250°, and can be desulphurised to hydurilic acid by heating at 100° with concentrated sulphuric acid. Hydurilic acid is most conveniently purified by precipitating the sparingly soluble copper salt from a solution of the neutral ammonium salt, and decomposing this with hot hydrochloric acid, in which the hydurilic acid is only slightly soluble (Baeyer, Annalen, 1863, 127, 15).

Hydurilic acid crystallises from hot water in small four-sided prisms containing $2H_2O$, or is precipitated as a fine crystalline powder containing $1H_2O$ by the addition of hydrochloric acid to a hot aqueous solution. It is sparingly soluble in alcohol or cold water, more readily so in hot water; its heat of combustion is 658·5 Cal. (Matignon, Ann. Chim. Phys. 1893, [vi.] 28, 328).

Hydurilic acid bears the same relation to dialuric and barbituric acids that alloxantin bears to alloxan and barbituric acid. Conrad (Annalen, 1907, 365, 24) has shown that its constitution is correctly represented by the formula



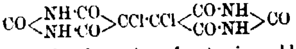
$$\mathrm{CO}<\begin{matrix}\mathrm{NH\cdot CO}\\\mathrm{NH\cdot CO}\end{matrix}>\mathrm{CH\cdot CH}<\begin{matrix}\mathrm{CO\cdot NH}\\\mathrm{CO\cdot NH}\end{matrix}>\mathrm{CO}$$

by its synthesis from ethyl ethanetetracarboxylate and carbamide (*v. supra*), and also by the fact that on hydrolysis with concentrated hydrochloric acid at 200°–230° it is converted almost quantitatively into carbon dioxide, ammonia, and succinic acid; barbituric acid when similarly treated yields carbon dioxide, ammonia, and acetic acid.

Hydurilic acid is not attacked by reducing agents; it yields alloxan and dibromobarbituric acid when treated with bromine water (Biltz, Heyn, and Hamburger, Ber. 1916, 49, 662).

Fuming nitric acid oxidises it into alloxan, whilst weaker acid converts it into nitrobarbituric acid (dilituric acid), *iso*nitrosobarbituric acid (violuric acid) and violantin. Ferric chloride or silver oxide oxidises it to oxyhydurilic acid, which gives a blood-red coloration with ferric chloride. Hydurilic acid has marked acidic properties, and decomposes most metallic chlorides and acetates, yielding the corresponding hydrogen hydurilate (for the basicity of the acid, *see* Biltz and Hamburger, Ber. 1916, 49, 655). The heat of neutralisation of hydurilic acid with 2 mols. potassium hydroxide is 21·8 Cal; but on adding a further quantity of alkali (up to 16 mols.) there is a further evolution of 4[illegible] of heat, thus pointing to the existence al. of [illegible] ble acid function. The following very few [illegible] described: the *ammonium hy*[illegible] ave been [illegible] small octahedral spa[illegible] $NH_4{\cdot}C_8H_5O_6N_4$, small octahedral acid [illegible] ble crystals precipitated by acetic acid; the *normal ammonium* salt [illegible] tions of the *normal ammonium* salt [illegible] which crystallises in needle[illegible] O_6N_4 which crystallises in needles [illegible] or in large monoclinic cryst[illegible] $_2O$, $a:b:c=1{\cdot}0821:1:0{\cdot}7003$. *Sodiu*[illegible] $H_4O_6N_4,4H_2O$ crystallises in prisms; [illegible] *hydrogen* salt $KC_8H_5O_6N_4$ forms sp[illegible] uble microscopic needles; the *norma*[illegible] $H_4O_6N_4,3H_2O$ is soluble and crystal[illegible] prisms (Matignon). The *calcium* salts [illegible] $N_4)_2,8H_2O$ and [illegible] $N_4,3H_2O$ are crystalline [illegible] the *barium* salt BaC_8[illegible] almost insoluble; the *zinc* salts $Zn(C_8H_5O_6N_4)_2$ a[illegible] H_2O; the [illegible] $C_8H_4O_6N_4,2H_2O$ ar[illegible] e crystalline; the *copp*[illegible] $Cu(C_8H_5O_6N_4)_2,8$[illegible] H_2O forms fine yellow [illegible] or prisms, which become red on heating [illegible] water. The *silver* salt is unstable; loss of w[illegible] salt is a dark green precipitate, and the formation of a dark green colour with ferric chloride is a characteristic reaction of the salts of hydurilic acid; the *ferrous* salt is white becoming green; the *lead* salt is insoluble in acetic acid.

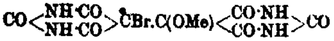
5 : 5′-*Dichlorohydurilic acid*



$$\mathrm{CO}<\begin{matrix}\mathrm{NH\cdot CO}\\\mathrm{NH\cdot CO}\end{matrix}>\mathrm{CCl\cdot CCl}<\begin{matrix}\mathrm{CO\cdot NH}\\\mathrm{CO\cdot NH}\end{matrix}>\mathrm{CO}$$

is obtained by the action of potassium chlorate on an intimate mixture of hydurilic and concentrated hydrochloric acids (Baeyer, Annalen, 1863, 127, 26); a quantitative yield is obtained by chlorinating hydurilic acid in alcohol, Biltz and Hamburger (*l.c.*). It is a sparingly soluble powder, soluble in concentrated sulphuric acid and precipitated therefrom by the addition of water, in small rhombic crystals containing $2H_2O$; it is readily decomposed by alkalis yielding the metallic chloride. The *potassium* salt $K_2C_8H_2Cl_2O_6N_4,2H_2O$ is a sparingly crystalline soluble powder.

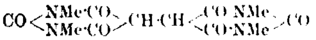
5-bromo-5′-methoxyhydurilic acid,



$$\mathrm{CO}<\begin{matrix}\mathrm{NH\cdot CO}\\ \mathrm{NH\cdot CO}\end{matrix}>\mathrm{CBr.C(OMe)}<\begin{matrix}\mathrm{CO\cdot NH}\\ \mathrm{CO\cdot NH}\end{matrix}>\mathrm{CO}$$

is formed on brominating hydurilic acid in presence of methyl alcohol; it crystallises in stout, hexagonal tablets which decompose above 360°; in presence of ethyl alcohol *5-bromo-5′-ethoxyhydurilic* acid is formed which crystallises in stout, elongated prisms decomposing above 360°: these compounds yield *5-methoxyhydarilic* acid and *5-ethoxyhydurilic acid* on reduction, which lose alcohol when heated and yield *dehydrohydurilic acid*: Biltz, Heyn, and Hamburger (Ber. 1916. 49, 662; *ibid.* 1919, 52 [B], 1298; *cf.* Baeyer, Annalen, 1863, 127, 26), who found that hydurilic acid broke down under the action of bromine water into dibromobarbituric acid and alloxan.

Tetramethylhydurilic acid (*deoxyamalic acid*) $C_{13}H_{14}O_6N_4$;



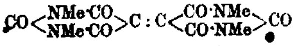
$$\mathrm{CO}<\begin{matrix}\mathrm{NMe\cdot CO}\\ \mathrm{NMe\cdot CO}\end{matrix}>\mathrm{CH\cdot CH}<\begin{matrix}\mathrm{CO\cdot NMe}\\ \mathrm{CO\cdot NMe}\end{matrix}>\mathrm{CO}$$

is obtained by the dry distillation of amalic acid (Fischer and Reese, Annalen, 1883, 221, 339), or more conveniently by heating it in a sealed tube for 3 hours at 180°–185° (Matignon, Compt. rend. 1893, 116, 642); has also been obtained by heating dimethyl*pseudo*uric acid with fused oxalic acid at 170° (Fischer and Ach, Ber. 1895, 28, 2473). Deoxyamalic acid is crystalline, has m.p. 260°, with decomposition and can be distilled, although with partial decomposition. It is almost insoluble in hot or cold water; readily soluble in chloroform or acetic acid; its heat of combustion is 1321·8 Cal. (Matignon, Ann. Chim. Phys. 1893, [vi.] 28, 327). Its chemical properties are similar to those of hydurilic acid, it reduces ammoniacal silver nitrate solution on warming, and gives a beautiful green coloration with ferric chloride; on gentle oxidation it yields a product that gives a blood-red coloration with ferric chloride; but when oxidised by nitric acid it forms dimethylalloxan.

5 : 5′-*Dichlorotetramethylhydurilic acid* may be obtained by chlorinating tetramethylhydurilic acid in alcohol; it forms transparent crystals with rectangular section, m.p. 266°. It is devoid of acidic properties, Biltz and Hamburger (*l.c.*).

5-bromo-5′-methoxy (or *ethoxy*) *tetramethylhydurilic acid* is formed on brominating tetramethylhydurilic acid in presence of methyl or ethyl alcohol. The bromomethoxy derivative forms elongated rhombic tablets and has m.p. 245°–247° (decomp.) and the bromoethoxy analogue forms elongated hexagonal tablets, m.p. 199°–200° (decomp.).

5 : 5′-*dibromotetramethylhydurilic acid* is formed by the action of bromine on tetramethylhydurilic acid in carbontetrachloride in complete absence of water; it crystallises in snow-white lancet-shaped leaflets and yields alkyloxy compounds on treatment with alcohols. It loses both atoms of bromine on heating at 140°–180°, forming *tetramethyldehydrohydurilic* acid



$$\mathrm{CO}<\begin{matrix}\mathrm{NMe\cdot CO}\\ \mathrm{NMe\cdot CO}\end{matrix}>\mathrm{C:C}<\begin{matrix}\mathrm{CO\cdot NMe}\\ \mathrm{CO\cdot NMe}\end{matrix}>\mathrm{CO}$$

a highly reactive compound which melts at 284°. With boiling methyl alcohol it forms *5-methoxy-tetramethylhydurilic* acid which crystallises in stout, four-sided prisms, m.p. 284° (decomp.).

5-aminotetramethylhydurilic acid

$$C_{12}H_{15}O_6N_5,H_2O$$

m.p. 295°–300° (decomp.) is prepared by acting upon *dehydrotetramethylhydurilic* acid with aqueous ammonia; it crystallises in silky rhombic leaflets. It is reduced by hydriodic acid and phosphonium iodide to 1 : 3-*dimethyluramil* and, on brominating it in alcohol, yields 5 : 5-dibromo-1 : 3-dimethyl barbituric acid.

5-methyl-amino-tetramethylhydurilic acid crystallises in rhombic plates.

5-anilinotetramethylhydurilic acid has m.p. 160°–161 (decomp.) and forms an aniline salt $C_{18}H_{19}O_6N_5,NH_2Ph$ which melts at 134°.

Deoxyamalic acid has only two acidic functions; the *potassium* $K_2C_{12}H_{12}O_6N_4$ and the *sodium* salt $Na_2C_{12}H_{12}O_6N_4$ are sparingly soluble (Matignon, *l.c.*; Fischer and Ach, *l.c.*).

For the preparation of *s*-dimethyl-hydurilic *acid* and derivatives, *see* Biltz and Heyn (Ber. 1919, 52 [B], 1298). M. A. W.

HYENANCHIN $C_{15}H_{18}O_7$. A substance, probably a dilactone, found in *Hyenanche globosa*, Lamb (*Toxicodendron capense*, Thun.), a member of the N.O. *Euphorbiaceæ*, growing in S. Africa. Existence of active principle first indicated by Henkel (Arch. Pharm. 1858, 144, 16), and first isolated by Engelhardt (Arb. Pharm. Inst. Dorp. 1892, 8, 5). Further investigated by Henry (Chem. Soc. Trans. 1920, 117, 1619), who gives details of its mode of extraction. Slender, colourless needles, or hexagonal prisms. When heated becomes yellow at 200°, then darkens and finally decomposes with effervescence at 234°. Slightly soluble in water, alcohol, ethyl acetate, or acetone. $[\alpha]_D^{15}$ +14·7° in water. Reduces Barreswil's (Fehling's) solution on boiling, decolorises permanganate solution and gives an amorphous yellow precipitate with bromine water.

Iso-Hyenanchin crystallises from boiling water in long, slender needles. Has no melting-point, and is decomposed at 299° with effervescence. Is less soluble in water than hyenanchin, but its solution also reduces Barreswil's solution. Both modifications are toxic, and resemble picrotoxin in action but are much weaker, especially the *iso*-variety. They are isomeric with picroton.

Hyenanche globosa contains also a saturated alcohol $C_{24}H_{49}\cdot OH$; minute needles, m.p. 82°–83° (corr.); a lævo-rotatory phytosterol, lustrous needles, m.p. 265° (corr.), readily soluble in chloroform or boiling ethyl acetate, sparingly so in alcohol, together with a yellow colouring matter; microscopic yellow needles, m.p. 270°–280° (decomp.), probably belonging to the flavone group (Henry, *l.c.*).

HYGRINES *v.* COCAINE.

HYMENODICTYONINE (*Hymenodictine*)

$$C_{23}H_{40}N_2,$$

crystals, m.p. 66°, occurs in the bark of *Hymenodictyon excelsum* (Wall.), used in India as an antipyretic. It is bitter and slightly toxic (Naylor, Pharm. J. 1883, [iii.] 13, 817; 1885, [iii.] 15, 195).

HYOSCINE *v.* TROPEINES.

HYOSCYAMINE and **HYOSCYAMUS** *v.* HENBANE; TROPEINES.

HYPAPHORINE v. Betaines.

HYPEROL. Trade name for a mixture of urea and hydrogen peroxide stabilised by a trace of citric acid.

HYPERSTHENE. A rock-forming mineral belonging to the orthorhombic series of the pyroxene group, and consisting of metasilicate of magnesium and iron $(Mg,Fe)SiO_3$. With less iron it passes isomorphously into bronzite and enstatite (*q.v.*). It is a common constituent of basic igneous rocks, especially norite. The very coarse-grained norite found as boulders on the coast of Labrador consists of labradorite (*v.* Felspar) and hypersthene, the former showing brilliant coloured reflections and the latter a bright coppery sheen. This material is therefore sometimes used as an ornamental or precious stone. The mineral is opaque, with a dingy, brownish-black body-colour, and the metallic reflection is due to the presence of minute crystalline enclosures arranged parallel to one plane. Sp.gr. 3·4. L. J. S.

HYPNAL v. Synthetic drugs.

HYPNOGEN. Syn. for veronal.

HYPNONE v. Ketones; Synthetic drugs.

HYPONITRITES v. Nitrogen.

HYPOPHOSPHITES v. Phosphorus.

HYPOPHYSIS v. Pituitary body.

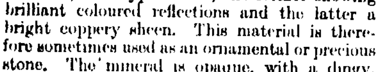
HYPOQUEBRACHINE v. Quebracho alkaloids.

HYPORIT. Trade name for calcium hypochlorite containing about 80 p.c. available chlorine, forming a stable powder which can be compressed into tablets of accurate dosage It is readily soluble in water, giving a faintly alkaline solution and may be used as a substitute for Dakin's solution as an antiseptic.

HYPOSCHROME v. Colour and chemical constitution.

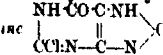
HYPOSULPHITES v. Sulphur.

HYPOXANTHINE or **SARCINE,** 6-*oxypurine*

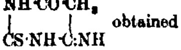


discovered by Scherer (Annalen, 1850, 73, 328) in milk, spleen, and blood, is widely distributed both in the animal and vegetable kingdoms. Strecker (Phil. Trans. 1858, 10, 121) isolated it from meat juice, and hence called it *sarcine*; it was afterwards found to be identical with Scherer's hypoxanthine (*see* Salkowski, Biochem. Zeitsch. 1913, 55, 250; Yoshimura, *ibid.* 1911, 37, 481). It is a normal constituent of bone marrow (Heymann, Pflüger's Archiv. 6, 184), glands, muscles, liver, brain (Salomon, Ber. 1878, 11, 574; Kossel, Chem. Zentr. 1881, 486; Buglia and Costantino, Zeitsch. physiol. Chem. 1913, 83, 45; Smorodinzew, Chem. Zentr. 1914, 2, 797), blood (Scherer, *l.c.*; Salomon, Chem. Zentr. 1878, 681; Bass, Arch. f. exp. Path. u. Pharm. 76, 40), and urine (Strecker, *l.c.*; Salomon, Zeitsch. physiol. Chem. 1887, 11, 410), the amount varying from 0·024 p.c. in the grey matter of the brain (Kossel, *l.c.*) to 0·218 p.c. in the calf's thymus (Schindler, Zeitsch. physiol. Chem 1889, 13, 432). Piccard found 5–8 p.c. of hypoxanthine and guanine in salmon roe (Ber. 1874, 7, 1714), whilst ox testis and the spermatozoa of carp contain 0·281 and 0·300 p.c. respectively of the former base (Schindler, *l.c.*). In the vegetable kingdom hypoxanthine occurs in beer yeast (Schutzenberger, Chem. Zentr. 1877, 73); in fungi (Winterstein and Jegorow, Landw. Versuchs. Stat. 79 and 80, 541; Buschmann, Pharm. Post. 45, 453, from Chem. Zentr. 1912, 2, 613); and in hops (Chapman, Chem. Soc. Trans. 1914, 105, 1895); potato juice to the extent of 0·0037 gram per 1 c.c. (Schulze, Landw. Versuchs. Stat. 1882, 28, 111); in the leaf buds of plane and maple, bark of plane, in lupines, young grass, red clover, oats, vetch, in sugar beet (Schulze and Bosshard, Zeitsch. physiol. Chem. 1885, 9, 420; Von Lippmann, Ber. 1896, 29, 2645). It is present in heated soils (Schreiner and Lathrop, J. Amer. Chem. Soc. 1912, 34, 1242; Schreiner and Shorey, J. Biol. Chem. 1910, 8, 385).

The chief source of hypoxanthine in the animal economy appears to be nucleic acid, which, under the action of certain tissue enzymes, most abundant in the liver and spleen, is decomposed: thus *nuclease* liberates the purine bases adenine and guanine, and these are further changed by the deamidising enzymes *adenase* or *guanase* into hypoxanthine and xanthine respectively, and finally *oxydases* convert hypoxanthine into xanthine and xanthine into uric acid (Halliburton, Chem. Soc. Reports, 1909, 168; Amberg and Jones, Zeitsch. physiol. Chem. 1911, 73, 407; Long, J. Biol. Chem. 1913, 15, 449). Salomon (Ber. 1887, 11, 574; 12, 95) obtained hypoxanthine from blood fibrin by the action of pancreas ferment, by simple decay, or by digestion with dilute hydrochloric acid (8 parts in 1000 parts of water); and Kossel (Zeitsch. physiol. Chem. 1881, 5, 152) found that the nuclein from pus cells and goose blood yielded on prolonged boiling 1·03 and 2·64 p.c. respectively of hypoxanthine. On the other hand, Leathes (J. Physiol. 1906, 35, 125, 205), Leonard and Jones (J. Biol. Chem. 1909, 6, 453), and Vögtlin and Jones (Zeitsch. physiol. Chem. 1910, 66, 250), have shown that uric acid excretion is related in some way to muscular exercise, and the most important purine base which contributes to the endogenous uric acid is muscular preformed hypoxanthine. According to Frank and Przedborski (Arch. exp. Path. u. Pharm. 68, 349) 50 p.c. of ingested hypoxanthine is utilised in the formation of uric acid. This is not directly connected with nuclein metabolism, since it may occur in the absence of adenase, an essential factor in the passage from nucleic acid to hypoxanthine. Hypoxanthine has therapeutic properties (Funk, J. of Physiol. 45, 489). It raises the blood pressure (Backmann, Zentr. blatt. f. Physiol. 26, 166; Degrez and Dorléans, Compt. rend. 1913, 156, 93).

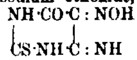
Fischer (Ber. 1897, 30, 2226; D. R. P. 1898, 17673) has synthesised hypoxanthine from trichloropurine by the following reactions: trichloropurine when heated with normal aqueous potassium hydroxide yields 6-*oxy*-2 : 8-*dichloropurine*  , which is reduced to hypoxanthine by the action of hydrogen iodide. Hypoxanthine is also obtained from adenine (6-*aminopurine*) by the action of nitrous acid, or from uric acid by reduction with alkali and chloroform (Sundvik, Zeitsch. physiol. Chem. 1897, 23, 476; 26, 13; *ibid.* 1912, 76, 486).

A further synthesis of hypoxanthine from ethylcyanacetate and thiourea is described by Traube (Annalen, 1904, 331, 64); *4-amino-6-hydroxy-2-thiopyrimidine*



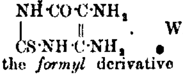
$$\begin{array}{l}\mathrm{NH{\cdot}CO{\cdot}CH_2}\\ \mathrm{|\qquad\quad|}\\ \mathrm{CS{\cdot}NH{\cdot}C{:}NH}\end{array}$$

obtained by the condensation of ethylcyanacate and thiourea in the presence of sodium ethoxide, forms an *isonitroso derivative*



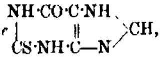
$$\begin{array}{l}\mathrm{NH{\cdot}CO{\cdot}C:NOH}\\ \mathrm{|\qquad\quad|}\\ \mathrm{CS{\cdot}NH{\cdot}C:NH}\end{array}$$

which on reduction yields *4 : 5-diamino-6-oxy-2-thiopyrimidine*



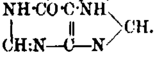
$$\begin{array}{l}\mathrm{NH{\cdot}CO{\cdot}C{\cdot}NH_2}\\ \mathrm{|\qquad\quad\ \|}\\ \mathrm{CS{\cdot}NH{\cdot}C{\cdot}NH_2}\end{array}$$

. When the sodium salt of the *formyl* derivative of this compound is heated at 250°–255° it is converted into *6-oxy-2-thiopurine*



$$\begin{array}{l}\mathrm{NH{\cdot}CO{\cdot}C{\cdot}NH}\diagdown\\ \mathrm{|\qquad\quad\ \|\qquad\quad\ \ CH}\\ \mathrm{CS{\cdot}NH{\cdot}C{-}N}\diagup\end{array}$$

, which loses its sulphur on treatment with dilute nitric acid (25 p.c.) at 100°, yielding hypoxanthine



$$\begin{array}{l}\mathrm{NH{\cdot}CO{\cdot}C{\cdot}NH}\diagdown\\ \mathrm{|\qquad\quad\ \|\qquad\quad\ \ CH.}\\ \mathrm{CH{:}N{-}C{-}N}\diagup\end{array}$$

Hypoxanthine is a white crystalline powder, crystallising in two modifications, one form consisting of needles containing water of crystallisation, which spontaneously and readily lose their water yielding anhydrous octahedra (Micko, Zeitsch. Nahr. Genussm. 1904, 8, 225); it decomposes without melting at 150°, and dissolves in 69·5 parts of boiling water or 1400 parts at 19° (Fischer, Ber. 1897, 30, 2226).

Hypoxanthine exhibits both acid and basic properties, and combines with one equivalent of an acid, or two equivalents of a base; the following *salts* are described: the *hydrochloride* $C_5H_4N_4O{\cdot}HCl,H_2O$, crystalline plates or needles, yields a sparingly soluble *platinichloride*

$$(C_5H_4N_4O{\cdot}HCl)_2{\cdot}PtCl_4$$

and a crystalline *aurichloride*

$$C_5H_4N_4O{\cdot}HCl.AuCl_3$$

the *hydrobromide* $C_5H_4N_4O{\cdot}HBr$ and *nitrate* $C_5H_4N_4O{\cdot}NHO_3$ are crystalline; the *picrate* dissolves in 450–500 parts of water at the ordinary temperature (Krüger and Salomon, Zeitsch. physiol. Chem. 1898, 26, 362). The *barium* derivative $C_5H_4N_4O{\cdot}Ba(OH)_2$ is crystalline, the *silver* salt $C_5H_2N_4OAg_2,H_2O$ loses $\frac{1}{2}H_2O$ at 100°; in the presence of excess of ammonia the salt crystallises with $3H_2O$, and loses $2\frac{1}{2}H_2O$ at 120°. The phosphotungstate forms straw-coloured cubical plates (Drummond, Biochem. J. 1918, 12, 5).

Hypoxanthine-d-glucoside crystallises in long needles, m.p. 245°, $[\alpha]_D^{20°}$ −34·5° in *N*/1-sodium hydroxide and +12·92° in *N*/1-hydrochloric acid solution (Fischer and Helferich, Ber. 1914, 47, 210).

Hypoxanthine forms characteristic sparingly soluble derivatives with certain metallic salts, and these are used for separating and estimating the base. The *compound* with *mercuric chloride* $C_5H_3N_4O,HgCl_2,H_2O$ is crystalline; the *compound* with *silver nitrate* $C_5H_4N_4O,AgNO_3$ is a flocculent precipitate, crystallising from hot nitric acid (sp.gr. 1·1), 1 part dissolves in 4960 parts cold nitric acid; according to Salkowski (Pflüger's Archiv. 4, 91), the presence of gelatin prevents the precipitation of hypoxanthine by silver nitrate; the *picrate* $AgC_5H_3N_4O,C_6H_2N_3O_7$, is a lemon-yellow crystalline salt, insoluble in cold water, precipitated from a hypoxanthine salt by sodium picrate and silver nitrate (Bruhns, Zeitsch. physiol. Chem. 1890, 14, 555).

Bromohypoxanthine $C_5H_3BrN_4O,2H_2O$ is sparingly soluble in cold water, and is obtained by the action of bromine (1 mol.) on hypoxanthine (1 mol.) at 120°, or by the action of sodium nitrite on a solution of bromadenine at 70°; on heating hypoxanthine for 6 hours at 100°–150° with excess of bromine, *bromohypoxanthine-tetrabromide hydrobromide* $C_5H_3BrN_4O{\cdot}HBr{\cdot}Br_4$ is obtained (Krüger, Zeitsch. physiol. Chem. 1894, 18, 449).

Urethane of hypoxanthine $C_5H_3N_4O{\cdot}COOEt$, prepared by the interaction of ethylchlorocarbonate and hypoxanthine, crystallises in plates, m.p. 185°–190°, and is sparingly soluble (Bruhns and Kossel, Zeitsch. physiol. Chem. 1892, 16, 1). Hypoxanthine combines with adenine to form the crystalline *compound*

$$C_5H_4N_4O{\cdot}C_5H_5N_5,3H_2O$$

(Bruhns, Ber. 1890, 23, 225); and like other purine derivatives containing an imino group in position 7 it yields coloured *derivatives* with diazobenzene salts (Burian, Ber. 1904, 37, 696).

Separation and estimation.—From mixtures of the xanthine bases, adenine and hypoxanthine are separated from xanthine and guanine by means of their sparingly soluble derivatives with silver nitrate in nitric acid solution. The mixed silver compounds are decomposed by hydrochloric acid, the filtrate nearly neutralised with sodium carbonate and the adenine precipitated as picrate. The filtrate is neutralised with ammonia, and the hypoxanthine precipitated with ammoniacal silver nitrate (Bruhns, Ber. 1890, 23, 225; *cp.* also Kossel, Zeitsch. physiol. Chem. 1883, 8, 404; Schindler, *ibid.* 1889, 13, 432; Krüger, *ibid.* 1894, 20, 170). M. A. W.

HYRGOL *v.* SYNTHETIC DRUGS.

HYRGOLUM. Trade name for a form of colloidal mercury.

HYSTARAZIN *v.* ALIZARIN AND ALLIED COLOURING MATTERS.

IACHIOL. Trade name for silver fluoride.

IBIT *v.* SYNTHETIC DRUGS.

IBOGA. A plant *Tabernanthe Iboga* (Baill.), natural order *Acanthaceæ*, found in the Congo, the root of which is chewed by the natives and which is said to possess properties similar to those of coca and kola. It enables persons to withstand fatigue, is used as a remedy for sleeping sickness and acts as an aphrodisiac.

Ibogaïne $C_{26}H_{32}O_2N_2$ (*Ibogine*), an alkaloid occurring in 'iboga' (*Tabernanthe Iboga*) obtained from the French Congo. Orthorhombic crystals m.p. 152°, lævo-rotatory (Dybowski and Landrin, Compt. rend. 1901, 133, 748; Haller and Heckel, *ibid.* 1901, 133, 850). The alkaloid produces anæsthesia, and in large doses causes convulsions and death due to stoppage of respiration (Lambert and Heckel, *ibid.* 1901, 133, 1236).

ICACIN *v.* Oleo-resins.

ICE BLACK *v.* Azo colouring matters.

ICE COLOURS. Colours formed on the fibre by treating it with a phenol and then with a diazotised amine in presence of ice. Known also as ingraine colours; *v.* Azo- colouring matters.

ICELAND MOSS. *Cetraria islandica.* Yields on extraction with ether *proto-α-lichesteric acid*, which when subjected to a temperature higher than 45° is converted more or less into *α-lichesteric acid* $C_{18}H_{30}O_5$, m.p. 124°, which again is converted into *dilichesteric acid.* Acetone extracts from Iceland moss the potassium salt of *fumaroprotocetraric acid*, which is readily split up into acid potassium fumerate and *cetraric acid*; the latter does not occur in the free state. The cold-water soluble carbohydrates of Iceland moss include *lichenin*, *d-lichenidin* $[\alpha]_D = +15{\cdot}4$, and *lichenoin* $C_{12}H_{20}O_{10}[\alpha]_D = +202{\cdot}7$, which on hydrolysis yields dextrose and a carbohydrate $C_6H_{10}O_5$, which gives a crystalline derivative with barium hydroxide. On boiling with water and a little sodium carbonate the lichen loses about 61 p.c., and the residue is largely hydrolysable by dilute acid, yielding mainly dextrose, some galactose and a very little mannose (Hesse, J. prakt. Chem. 1916, 94, 227; J. Soc. Chem. Ind. 1917, 566); *v.* Lichens.

ICELAND-SPAR *v.* Calcite; Calcium.

ICE-SPAR *v.* Cryolite.

ICHTHALBIN. Syn. for ichthyol albuminate.

ICHTHARGAN *v.* Synthetic drugs.

ICHTHERMOL. Trade name for a mercury compound of ichthyol.

ICHTHOFORM. Trade name for a combination of ichthyol and formaldehyde. Used as an intestinal antiseptic.

ICHTHOSULPHOL (*ichthynal*). Syn. for ichthyol (*q.v.*).

ICHTHYOL. A pharmaceutical product distilled from fossilised fish remains, found in the Tyrol and on the coasts of the Adriatic. Similar deposits are found in the valley of the Isar and the Loisach; in Switzerland north of Meride, and in various parts of Italy.

Crude ichthyol from the Seefeld district between Southern Bavaria and the Tyrol has long been used as an antiseptic remedy. The crude 'rock oil' is obtained by simple distillation from the shale or 'stinkstein,' a bituminous substance of a grey or black colour occurring in the upper dolomites. The amount of oil obtained varies from 1 to 10 p.c. An installation of nine stills yields, on an average, 15 to 20 kilos. of oil per charge. In one works the output of crude oil is over 3000 kilos. per annum. As found in pharmacy, the substance consists mainly of the ammonium sulphonate. It is not a simple substance but a mixture of ammonium ichthyol sulphonate with about 1 p.c. of a powerful-smelling empyreumatic oil, 5 to 7 p.c. of ammonium sulphate, and about 50 p.c. water.

According to Baumann and Schotten, ichthyol-sulphonic acid has the formula

$$C_{28}H_{36}S(SO_2OH)_2$$

An odourless ichthyol has been prepared by Knorr & Co. which has the therapeutic activity of the original strong-smelling product (J. Soc. Chem. Ind. 1903, 1304; 1910, 44, 174, 264).

The purification of the crude oil is effected by heating it with soda lime, washing with dilute sulphuric acid, drying and heating with sodium in a current of ammonia gas. It then contains only a small quantity of a ketonic substance from which it may be freed by magnesium methyl chloride. After fractionation over sodium it becomes colourless and acquires a pleasant, fragrant smell (Scheibler, Ber. 1919, 52, 1903). According to the same authority (Archiv. et Pharm. 258, p. 70), the typical sulphur compounds of ichthyol and similar tar oils are derivatives of thiophen.

For ichthyol preparations *v.* Synthetic drugs.

ICHTHYOLIDIN. Trade name for piperazine ichthyolate.

ICHTHYOL-SALICYL. Trade name for a mixture of ichthyol and sodium salicylate.

ICICA and **ICACIN** *v.* Oleo-resins.

ICOSANE $C_{20}H_{42}$. A hydrocarbon found in paraffin. M.p. 36°; b.p. (under 15 mm. pressure) 205°; sp.gr. 0·778 at 37°/4°. Formed by the action of sodium on normal decyl iodide.

ICOSONENE *v.* Resin oil.

IDAEIN *v.* Anthocyanins.

IDOCRASE *v.* Vesuvianite.

IDRYL *v.* Fluoranthene.

IGNATIUS BEANS *v.* Nux vomica.

IGNOTINE *v.* Carnosine.

ILEX VOMITORIA (Aiton). The leaves of this tree growing in the South Eastern States of America, and used by the Indians, under the name of 'Yaupon' on account of their medicinal and stimulating properties, have been found by Power and Chesnut (J. Amer. Chem. Soc. 1919, 41, 1307) to contain notable amounts of caffeine.

ILICIC and **ILICYLIC ALCOHOLS** *v.* Bird-lime.

ILLIPÉ-NUT FAT. Illipé-nuts yield a considerable quantity of a fat which is imported from the Dutch East Indies, and used in conjunction with palm-kernel oil in the manufacture of candles. It is well adapted for the saponification method of stearin manufacture. In the autoclave it yields about 10 p.c. of glycerol of 28°B. (J. Soc. Chem. Ind. 1898, 161, 358); *v.* Bassia oil.

ILMENITE, or titaniferous iron-ore. A common mineral with approximately the formula $FeTiO_3$, but of variable composition. Analyses show TiO_2 22–59, FeO 20–46, Fe_2O_3 1–59 p.c. In its rhombohedral crystalline form it shows a close agreement with hæmatite, and it has consequently, until recently, been regarded as an isomorphous mixture of ferric oxide and titanium sesquioxide, the formula being written as an oxide $(Fe,Ti)_2O_3$. The discovery of the rhombohedral titanates of magnesium and manganese, geikielite ($MgTiO_3$) and pyrophanite ($MnTiO_3$), and the frequent presence of magnesium (and manganese) in ilmenite, suggest, however, that the mineral is really a titanate of ferrous iron, $FeTiO_3$ (S. L. Penfield, Amer. J. Sci. 1897, 4, 108). In the variety *picroilmenite* a considerable amount of iron is replaced by magnesium, the formula then being $(Fe,Mg)TiO_3$ (T. Crook and B. M. Jones, Min. Mag. 1906, 14, 165).

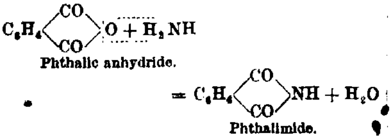
Ilmenite is black with a sub-metallic lustre, and often a smooth and lustrous conchoidal fracture, sp.gr. 4·5–5; H. 5–6. The massive mineral somewhat resembles magnetite in appearance, from which it is readily distinguished by its feeble magnetic character. It is of constant occurrence as isolated grains in the more basic igneous rocks (gabbro, diabase, basalt, &c.); and in certain instances it forms rich segregations in such rocks. Enormous deposits of ilmenite are found under these conditions at several places in Norway, Sweden, Canada, and the United States. With the weathering and breaking down of these igneous rocks, grains of ilmenite (*Manaccanite*, from Manaccan in Cornwall) collect in the beds of streams, sometimes forming considerable deposits of 'black iron-sand.'

Although large deposits of ilmenite are available for mining, the mineral has not yet found any important applications. It has been used for the preparation of titanium paints and enamels; and in the future it may be more utilised for the manufacture of titanium-steel, which possesses great ductility and a high limit of elasticity. (*See* J. T. Singewald, The Titaniferous Iron Ores of the United States, their Composition and Economic Value, U.S. Bureau of Mines, 1913, Bull. 64.) L. J. S.

ILMENORUTILE *v.* Strüverite.

ILVAITE, LIEVRITE, or **YENITE.** Acid silicate of iron and calcium, $HCaFe''_2Fe'''Si_2O_9$, crystallised in the orthorhombic system. It contains theoretically FeO 35·2, Fe_2O_3 19·6 p.c. (Fe 41 p.c.), but the ferrous oxide is partly replaced by an equivalent amount of manganous oxide (up to 8·6 p.c.). Sp.gr. 3·9–4·1, H. 5½–6; gelatinises with hydrochloric acid. The mineral is found somewhat abundantly as brilliant black crystals and as compact masses in the iron mines at Rio Marina and Cape Calamita in Elba. It is also known from Campiglia Marittima in Tuscany, Hebron in Nassau, British Columbia, Greenland, and Japan. L. J. S.

IMIDES. Nitrogenous compounds obtained by the action of gaseous ammonia on the anhydrides of dibasic acids and resulting in the substitution of the bivalent $>NH$ group (imidogen) for the oxygen atom uniting the two carbonyls, *e.g.*:



$$C_6H_4\left<\begin{matrix}CO\\CO\end{matrix}\right>O + H_2NH$$

Phthalic anhydride.

$$= C_6H_4\left<\begin{matrix}CO\\CO\end{matrix}\right>NH + H_2O$$

Phthalimide.

β-IMINAZOLYETHYLAMINE *v.* Ergot.

IMINES. Bases derived from aldehydes or ketones by the substitution of $>NH$ (imidogen) for oxygen. Imines derived from aldehydes are known as *aldimines*; those derived from ketones are called *ketimines*.

IMOGEN, eikonogen modified by the introduction of another amino group; used as a photographic developer.

IMPERIALINE $C_{35}H_{60}NO_4$. An alkaloid discovered by K. Fragner in *Fritillaria Imperialis* (Linn.). Short needles, m.p. 254° (approx.) $[\alpha]_D -35·4°$ in chloroform; yields a crystalline hydrochloride (Ber. 1885, 21, 3284). It is a heart-poison, and is probably closely related to the older alkaloid *Tulipine*, discovered by Gerard in *Tulipa Gesneriana* (Linn.).

IMPERIAL GREEN. *Emerald Green v.* Pigments.

IMPERIAL SCARLET *v.* Azo- colouring matters.

IMPERIAL YELLOW *v.* Aurantia.

INACTIVE CAMPHOR *v.* Camphors.

INCANDESCENT MANTLES *v.* Gas mantles.

INCARNATRIN *v.* Glucosides.

INCENSE, *see* **Olibanum**, art. Gum-resins; Oleo-resins.

INDACONITINE *v.* Aconitine.

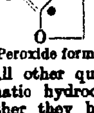
INDALIZARIN *v.* Oxazine colouring matters.

INDAMINES and **INDOPHENOLS.**

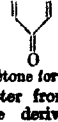
Constitution and mode of formation.—The indamines and indophenols are colouring matters most of which are too unstable to be of great practical value, but many of them are interesting as intermediate products in the manufacture of other more important dyestuffs. From a theoretical point of view they can claim great importance, as they form the starting-point of the modern 'quinonoid' structural formulæ now universally adopted for the majority of colouring matters. This is due to the fact that the indamines and indophenols are the simplest real colouring matters derived from the quinones, which are now considered as prototypes of chromogens.

All aromatic hydrocarbons are capable of forming quinonoid derivatives by the displacement of 2 hydrogen atoms by 2 atoms of oxygen. These may stand either in *o*- or in *p*-position to each other, whilst no quinones have ever been discovered which contain the oxygen atoms in *m*- position. The divalent nature of oxygen forces us to consider the quinones either as peroxides of aromatic hydrocarbons or as alicyclic diketones. The first of these possibilities was formerly considered as more probable and was made the basis of this article in the first edition of this dictionary. Since then the diketone formula has come to be generally adopted and it will therefore have to be used in this revision of the article.

The following formulæ represent the two different constitutions which may be given to *p*-quinone, the prototype of all the substances to be mentioned in this article:



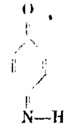
Peroxide formula.

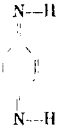


Diketone formula.

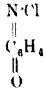
All other quinones, no matter from what aromatic hydrocarbon they are derived and whether they belong to the *o*- or *p*- series, may be similarly formulated and neither of these two different constitutions can be claimed as undoubtedly preferable to the other. It is very probable that the quinones are tautomeric and possessed of both constitutions according to the circumstances under which they react.

If the oxygen of *p*-quinone be replaced by divalent imino groups =NH, two compounds may be obtained, *p*-quinoneimide and *p*-quinonediimide, which for many years have been considered as hypothetical but have recently been prepared by Willstatter (Ber. 37, 1494, 4605). They are very unstable substances the constitution of which is expressed by the following formulæ (based, as all the subsequent formulæ of this article, on the diketonic constitution of the quinones)

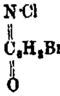

p-Quinoneimide

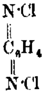

p-Quinonediimide

The iminic hydrogen of these compounds may be replaced by halogen atoms, and we thus obtain substances of a comparatively stable nature which have been known for a long time and may be used for the preparation of various derivatives. It was by treating quinonedichlorodiimide, dissolved in ether, absolutely free from moisture, with the theoretical quantity of dry hydrogen chloride that Willstatter first succeeded in preparing *p*-quinonediimide. Later on he found a general method for the production of both these imides in the oxidation of either *p*-phenylenediamine or *p*-aminophenol with dry silver oxide. They are slightly basic substances, capable of forming unstable hydrochlorides. In a free state they are white, but they resemble quinone in their reactions. Their great tendency to polymerisation is the cause why previous attempts at their isolation have failed.

Quinonechloroimide  $\begin{matrix}N\cdot Cl\\ \|\\ C_6H_4\\ \|\\ O\end{matrix}$ has been obtained by Schmitt and Bennewitz (J. pr. Chem. [ii.] 8, 2). It is prepared by allowing a solution of 43 grams *p*-aminophenol hydrochloride in 500 c.c. water and 100 c.c. concentrated hydrochloric acid to flow into a solution of sodium hypochlorite prepared by introducing 35 grams of chlorine into an ice-cold solution of 45 grams sodium hydroxide. The imide settles out and may be recrystallised from light petroleum (Willstätter, Ber. 37, 1499). It forms yellow crystals, melting at 85°; it is slightly explosive, volatile with aqueous vapour, and resembles quinone in many of its properties.

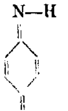
Trichloroquinonechloroimide $\begin{matrix}N\cdot Cl\\ \|\\ C_6HCl_3\\ \|\\ O\end{matrix}$ is prepared in the same manner from trichloraminophenol hydrochloride (Schmitt and Andresen, J. pr. Chem. [ii.] 23, 438; 24, 429). Yellow needles, m.p. 118°, similar to quinonechloroimide.

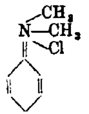
Dibromoquinonechloroimide  $\begin{matrix}N\cdot Cl\\ \|\\ C_6H_2Br_2\\ \|\\ O\end{matrix}$ is obtained by adding a solution of bleaching-powder to an aqueous acidulated solution of the double salt of dibromaminophenol hydrochloride and tin chloride. It separates in flesh-coloured crystals, melting at 80° (R. Möhlau, Ber. 16, 2845).

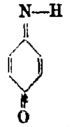
Quinonedichlorodiimide  $\begin{matrix}N\cdot Cl\\ \|\\ C_6H_4\\ \|\\ N\cdot Cl\end{matrix}$ is formed by acting with a solution of bleaching-powder upon a solution of *p*-phenylenediamine hydrochloride (Krause, Ber. 12, 47). Willstätter (Ber. 37, 1498) prepares it by allowing a solution of 54 grams *p*-phenylenediamine hydrochloride in 120 c.c. hydrochloric acid and 600 c.c. water to flow into a hypochlorite solution prepared by introducing 75 grams of chlorine into the solution of 90 grams sodium hydroxide in 500 c.c. of water. The imide separates in whitish flakes and may be recrystallised from light petroleum. White needles, insoluble in water, soluble in alcohol, benzene, &c., and exploding at 126°.

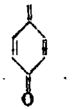
Quinonedibromodiimide $\begin{matrix}N\cdot Br\\ \|\\ C_6H_4\\ \|\\ N\cdot Br\end{matrix}$ may be prepared by acting with bromine water upon *p*-phenylenediamine hydrochloride (Krause, Ber. 12, 50). It is similar to the chloro derivative, and explodes at 86°.

These substances are not colouring matters, as may be seen from the above description. They cannot be colouring matters, because they are indifferent, whilst every dyestuff must be either an amine or a phenol (Witt, Bau und Bildung farbender Kohlenstoffverbindungen, Ber. 9, 522). Their chromophoric character, however, becomes apparent in those of their derivatives which are endowed with either basic or acid properties. Nitrosodimethylaniline and nitrosophenol, which, as their constitutional formulæ show, are closely related to quinonediimide and quinoneimide:


Quinonediimide.


Quinonedimethylaminooxime chloride (Nitrosodimethylaniline hydrochloride).

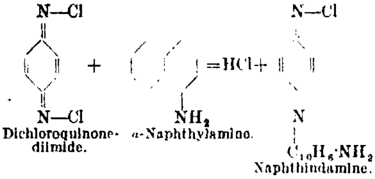

Quinoneimide.


Quinoneoxime (Nitrosophenol).

are by virtue of their basic and phenolic nature, colouring matters possessing some affinity for fibres, although they have no practical value as dyestuffs.

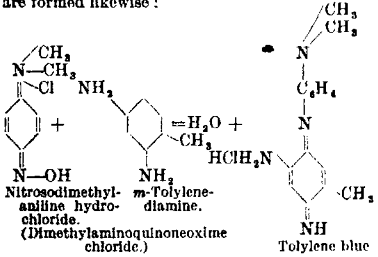
We may, however, obtain real colouring matters, many of which have proved useful and interesting, by preparing substitution products of the quinoneimides in which the substituting radicle is attached to nitrogen. Such products may be prepared by acting with amines or phenols upon quinoneimides, or their equivalents, quinonamidoximes (nitroso bases) and quinoneoximes (nitrosophenols). Various cases may here be cited:

1. By acting with aromatic amines upon quinonedichlorodiimides, indamines are formed, thus:



Dichloroquinone-diimide. α-Naphthylamine. Naphthindamine.

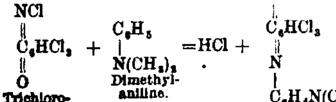
2. By acting with aromatic amines upon quinone-amidoximes (nitroso bases) indamines are formed likewise:



Nitrosodimethylaniline hydrochloride. (Dimethylaminoquinoneoxime chloride.) *m*-Tolylenediamine. Tolylene blue.

In this case, as in many similar ones in this group, the quinonoid character may in the formation of the dyestuff be shifted from one benzene ring to the other. This has been indicated in the formula, although we have no positive proof that such shifting takes place in the formation of tolylene blue.

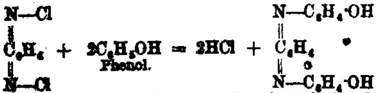
3. By acting with aromatic amines upon quinonechloroimides normal indophenols are formed:



$$\mathrm{ClN{=}C_6HCl_3{=}O + C_6H_5{-}N(CH_3)_2 = HCl + O{=}C_6HCl_3{=}N{-}C_6H_4N(CH_3)_2}$$

Trichloroquinonechloroimide. Dimethylaniline. Dimethyltrichlorobenzindophenol.

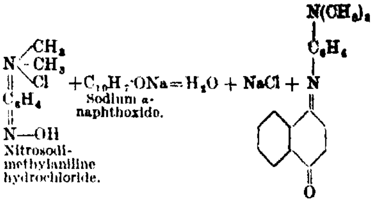
4. By acting with phenols upon quinonedichlorodiimides indophenols of a more complicated nature may be formed:



$$\mathrm{ClN{=}C_6H_4{=}NCl + 2C_6H_5OH = 2HCl + HO{\cdot}C_6H_4{-}N{=}C_6H_4{=}N{-}C_6H_4{\cdot}OH}$$

Quinonedichlorodiimide. Phenol. Complex indophenol.

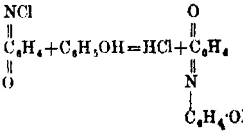
5. By acting with phenols upon quinonamidoximes (nitroso bases) normal indophenols are formed:



Normal naphthindophenol.

In this case again, as in No. 2, a migration takes place and the quinonoid nature is shifted from the benzene to the naphthalene nucleus. This can be proved to be the case by the fact that the resulting dyestuff is a weak base but entirely devoid of phenolic properties. It cannot therefore contain an OH group.

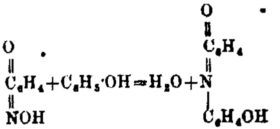
6. By acting with phenols upon quinonechloroimides colouring matters are formed, which although practically belonging to the indophenols are distinguished by the presence of a free hydroxyl group, by which they assume phenolic properties, dissolve in alkalis and have therefore been designated by the name of 'acid indophenols.'



$$\mathrm{ClN{=}C_6H_4{=}O + C_6H_5OH = HCl + O{=}C_6H_4{=}N{-}C_6H_4{\cdot}OH}$$

Quinonechloroimide. Acid indophenol, soluble in alkalis.

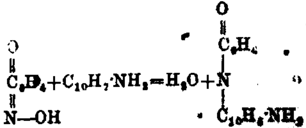
7. The same result takes place if the equivalents of quinoneimide, viz. the quinoneoximes or nitrosophenols be acted upon with phenols:



$$\mathrm{O{=}C_6H_4{=}NOH + C_6H_5{\cdot}OH = H_2O + O{=}C_6H_4{=}N{-}C_6H_4OH}$$

Quinoneoxime (nitrosophenol). Phenol. Acid indophenol, soluble in alkalis.

8. If, however, amines be acted upon with nitrosophenols, a normal indophenol is the result:

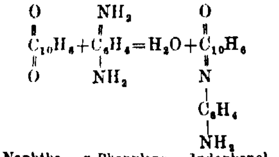


$$\mathrm{O{=}C_6H_4{=}N{-}OH + C_{10}H_7{\cdot}NH_2 = H_2O + O{=}C_6H_4{=}N{-}C_{10}H_6{\cdot}NH_2}$$

Nitrosophenol. α-Naphthylamine. Indophenol, insoluble in alkali.

9. The quinones themselves may be utilised for the production of these dyestuffs by being

acted upon with suitable diamines or aminophenols:



$$O{=}C_{10}H_6{=}O + NH_2{-}C_6H_4{-}NH_2 = H_2O + O{=}C_{10}H_6{=}N{-}C_6H_4{-}NH_2$$

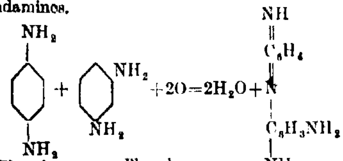
Naphthaquinone *p*-Phenylenediamine Indophenol.

This reaction makes it evident that the indamines and indophenols are nothing else than a certain group of the larger family of quinone anilides, viz. those of these anilides which contain the auxochromic groups necessary for developing their nature as dyestuffs.

For the production of indamines and indophenols it is, however, not necessary to start from ready-formed quinones, quinoneimides, diimides, or quinoneoximes. It is possible to prepare these substances by the joint oxidation of amines or phenols with compounds which are capable of producing a quinoneimide or diimide.

In this process we may assume that the hypothetical quinoneimides and -diimides are formed as intermediate products which immediately react upon the amines or phenols present in the mixture, forming indamines or indophenols, as the case may be. Every *p*-aminophenol or *p*-diamine is capable of being used for this reaction, and a large variety of colouring matters may thus be produced. The following combinations may take place:

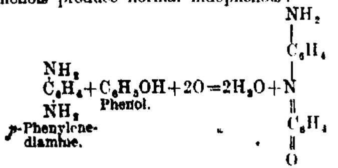
10. *p*-Diamines simultaneously oxidised **with aromatic amines give rise to the formation of indamines.**



$$C_6H_4(NH_2)_2 + C_6H_4(NH_2)_2 + 2O = 2H_2O + HN{=}C_6H_4{=}N{-}C_6H_3NH_2{-}NH_2$$

p-Phenylenediamine. *m*-Phenylenediamine Indamine (phenylene-violet).

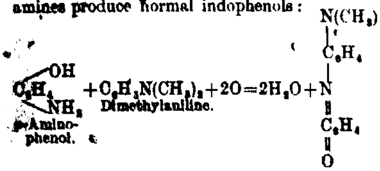
11. ***p*-Diamines** oxidised with aromatic **phenols** produce normal indophenols:



$$NH_2{-}C_6H_4{-}NH_2 + C_6H_5OH + 2O = 2H_2O + NH_2{-}C_6H_4{-}N{=}C_6H_4{=}O$$

p-Phenylenediamine. Phenol. Typical indophenol.

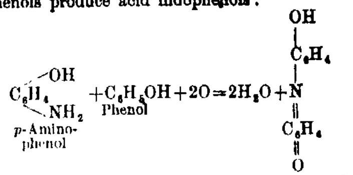
12. *p*-Aminophenols oxidised with aromatic amines produce normal indophenols:



$$C_6H_4(OH)(NH_2) + C_6H_5N(CH_3)_2 + 2O = 2H_2O + (CH_3)_2N{-}C_6H_4{-}N{=}C_6H_4{=}O$$

p-Aminophenol. Dimethylaniline. Indophenol.

13. ***p*-Aminophenols oxidised with aromatic phenols produce acid indophenols:**

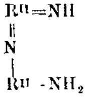


$$C_6H_4(OH)(NH_2) + C_6H_5OH + 2O = 2H_2O + HO{-}C_6H_4{-}N{=}C_6H_4{=}O$$

p-Aminophenol Phenol Acid indophenol.

From the above it will be seen that all the various colouring matters prepared by these reactions and built up on the quinone type may be subdivided into three varieties:—

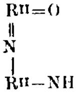
a. True *indamines* containing no oxygen, and having the generic formula:



$$HN{=}R^{II}{=}N{-}R^{II}{-}NH_2$$

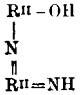
strong bases, forming stable salts with mineral acids.

b. Normal indophenols, containing oxygen in their chromophoric group; being amino derivatives of substituted quinoneimides of the generic formula:



$$O{=}R^{II}{=}N{-}R^{II}{-}NH_2$$

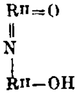
very weak bases, incapable of forming stable salts. With these the hydroxy derivatives of quinonediimides:



$$HO{-}R^{II}{-}N{=}R^{II}{=}NH$$

are practically identical, being transformed into normal indophenols *in statu nascendi* by the shifting or migrating process already mentioned.

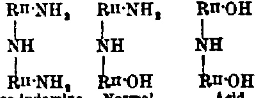
c. Acid indophenols, hydroxyl derivatives of quinonimides of the generic formula:



$$O{=}R^{II}{=}N{-}R^{II}{-}OH$$

distinct phenols, dissolving in caustic **alkali** solutions with intense colorations.

Like **all** colouring matters the **indamines** and indophenols are capable of being **reduced** by the action of nascent hydrogen, of which two atoms are taken up. Colourless 'leuco-' compounds are formed which stand in the **same** relation to the original dyestuff **as hydro**quinone stands to quinone:



$$R^{II}(NH_2){-}NH{-}R^{II}(NH_2) \qquad R^{II}(NH_2){-}NH{-}R^{II}(OH) \qquad R^{II}(OH){-}NH{-}R^{II}(OH)$$

Leuco-indamine. Normal leuco-indophenol. Acid leuco-indophenol.

It will be clearly seen that these formulæ of the leuco derivatives are identical with the

formulæ of paradiamino, aminohydroxy, and *p*-dihydroxy derivatives of secondary aromatic bases. Now as the leuco derivatives of indamines and indophenols are capable of reoxidation into the original dyestuff, it is apparent that we have by this means three additional methods for the production of such colouring matters:

14. Di-*p*-amino derivatives of secondary aromatic bases may be oxidised into indamines.

15. *p*-Amino-*p*-hydroxy derivatives of secondary aromatic bases may be oxidised into normal indophenols.

16. Di-*p*-hydroxy derivatives of secondary aromatic bases may be oxidised into acid indophenols.

The conditions under which these various reactions should be performed are stated below.

The remarkable relations existing between dyestuffs and their leuco compounds were recognised and studied by chemists at an early period. In no group are they so clearly defined as in that of the indamines and indophenols. Their complete elucidation in this group very naturally sheds light upon analogous phenomena observed in other colouring matters, and thus the study of this class of substances greatly facilitated the introduction of the modern views of the 'quinonoid' constitution of colouring matters.

Literature on the Constitution of Indamines and Indophenols, Otto N. Witt, J. Soc. Chem. Ind. 1882, 255; R. Mohlau, Ber. 16, 2843; Otto N. Witt, British Association, 1887; Journ. Soc. Dy. Col. 1887; R. Nietzki, Organische Farbstoffe, 5th ed. 1906, 197 *et seq.*

History.—The first indamine observed was the intermediate product obtained in the production of safranine, of which, however, no account was published. In 1879, Otto N. Witt prepared the first indamine in a state of purity by acting with nitrosodimethylaniline hydrochloride upon *m*-tolylenediamine (Ber. 12, 931; Chem. Soc. Trans. 1879, 1, 356). In 1881, Otto N. Witt and Horace Köchlin obtained patents for the production of normal indophenols. The production of 'acid indophenols' by the reaction of quinonechloroimide upon phenol was first mentioned by Hirsch (Ber. 13, 1909), and discussed by Möhlau (*ibid.* 16, 2845). The normal indophenols only have found a practical application in dyeing and calico-printing. Owing, however, to their insufficient resistance to the action of acids and to the difficulties in their application, they did not make very rapid progress in the favour of practical dyers and colourists. A change for the better took place, when it was shown that the typical indophenol is a good vat-dye and capable of being used in combination with indigo. The consumption of indophenol became considerable for a while, but went down again as rapidly as it had gone up when the introduction of synthetic indigo lowered the prices of this 'king of dyestuffs' and the invention of many indigoid colouring matters overwhelmed the dyer with dyes suitable for the vat-process.

In later years some of the indophenols have become important as raw materials for the production of some valuable sulphur dyes, which are prepared from them by the well-known process of boiling or melting with alkaline sulphides. This new application of the indophenols had been first indicated in D. R. P. 132212 of the Gesellschaft für Chemische Industrie, in Basle (14 Dec. 1898), and the corresponding Fr. Pat. 284387 and Amer. Pat, 665547.

Properties.—The properties of the indamines and indophenols are more uniform than those of other classes of colouring matters. It has consequently been necessary to prepare only a small number from the host of possible members of this group in order to obtain a fair notion of the properties of the whole group. With very few exceptions their shade is blue or violet; in some cases a bluish-green. The shade of the dyestuff is exhibited:

a. In the indamine group by the normal salts of the indamine bases.

b In the group of normal indophenols by the free bases.

c. In the group of acid indophenols by the alkaline salts of the dyestuffs.

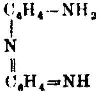
All the indamines and indophenols possess the generic character of the quinone group. They are therefore capable of acting as oxidising agents if brought together with oxidisable substances. In such reactions they take up hydrogen and are transformed into their leuco derivatives. So considerable is their tendency to act as oxidising agents that, under suitable conditions, an indamine or indophenol will attack its own molecules, when a mixture of its oxidation products and its leuco compounds is the result (*v. Safranines*, art. AZINES). The conditions under which such reactions take place are, an elevated temperature and the presence of mineral acids. The indamines and indophenols are consequently unstable in the presence of acids, whilst in alkaline and neutral solution they display but little tendency to decompose. A similar decomposition is caused, especially in the indamines, by the action of sunlight; the normal indophenols may, on the contrary, be called rather fast.

The following is an account of those members of this group of dyestuffs which have been more closely examined or proved important from a technical point of view:—

I. Indamines.

Phenylene-blue $C_{12}H_{11}N_3$

Constitution



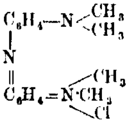
$$\begin{array}{l} C_6H_4-NH_2 \\ \quad | \\ \quad N \\ \quad \| \\ C_6H_4=NH \end{array}$$

This compound is best prepared by oxidising a mixture of *p*-phenylenediamine and aniline hydrochloride in equal molecules in the cold, with the theoretical quantity of potassium dichromate. A greenish-blue liquid is formed, from which the iodide of phenylene-blue may be precipitated by the addition of potassium iodide solution. This salt forms long needles with a green metallic lustre. It is soluble in water with a greenish-blue colour, which turns into green on the addition of mineral acids. Acid solutions decompose very rapidly, a considerable quantity of *p*-quinone being formed in this decomposition. On reduction phenylene-blue yields di-*p*-aminodiphenylamine, from which phenylene-blue may be regenerated by simple oxidation. Phenylene-blue is transformed into safranine on being boiled in a neutral solution with aniline hydrochloride (*v. Safranine*).

Literature.—R. Nietzki, Ber. 1883, 16, 464; R. Nietzki, Organ. Farbstoffe, 5th ed. 1906, 200.

Tetramethyl derivative of Phenylene-blue *Dimethylphenylene-green*).

$C_{16}H_{20}N_3Cl$. Constitution



$$\begin{array}{l} C_6H_4-N\begin{smallmatrix}CH_3\\ CH_3\end{smallmatrix} \\ \;| \\ N \\ \;\| \\ C_6H_4=N\begin{smallmatrix}CH_3\\ CH_3\\ Cl\end{smallmatrix} \end{array}$$

This interesting compound, which is the completely methylated derivative of the preceding one, is formed by the joint oxidation of *asym*-dimethyl-*p*-phenylenediamine with dimethylaniline, in equal molecules, with potassium dichromate in the presence of zinc chloride (Bindschedler, Ber. 13, 207). The zinc double salt is at once deposited from the liquid. According to the quantity of zinc chloride present the crystals are either of a copper colour or have a metallic green lustre. These crystals are freely soluble in pure water, with a fine green coloration. Potassium iodide precipitates from this solution the phenylene-green iodide $C_{16}H_{20}N_3I$ in beautiful green needles, which are easily soluble in pure water, very insoluble in the presence of an excess of potassium iodide. The platinum double chloride has the composition $(C_{16}H_{20}N_3Cl)_2PtCl_4$; dimethylphenylene-green is more stable than the majority of indamines. On reduction it yields tetramethyldiaminodiphenylamine from which the green may be regenerated by oxidation.

Dimethylphenylene-green dyes silk and other fibres a yellowish shade of green. It has, however, found no application as a colouring matter, being rather unstable to light.

Its solution, on being boiled with the solution of an equal molecule of the hydrochloride of a primary amine, yields the corresponding safranine. (Also *Safranine*.)

Literature.—Bindschedler, Ber. 13, 207; R. Nietzki, *ibid.* 16, 464; Bindschedler, *ibid.* 16, 865.

Diethylphenylene-green $C_{20}H_{28}N_3Cl$ is obtained by oxidising diethyl-*p*-phenylenediamine with diethylaniline in the presence of mercuric chloride. Very similar to the methyl derivative, but less stable.

Literature.—Bindschedler, Ber. 16, 867.

Homologues of phenylene-blue. These are formed by the joint oxidation of *p*-phenylenediamine and the homologues of aniline or of *p*-tolylenediamine with aniline and its homologues. They play an important part in the manufacture of the commercial safranines, in which they are obtained as intermediate products.

Literature.—O. N. Witt, J. Soc. Chem. Ind. 882, 256.

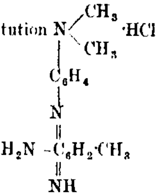
Witt's phenylene-violet $C_{12}H_{12}N_4$·HCl. This substance is obtained by the joint oxidation of *p*-phenylenediamine with *m*-phenylenediamine. Its aqueous solution, which exhibits a fine purple shade, is decomposed on boiling, when a corresponding diamino-azine or eurhodine is formed. Similar compounds are obtained by the joint oxidation of other *p*-diamines with *m*-phenylenediamine. This reaction is, therefore, applicable as a test for both *p*- and *m*-diamines.

Witt's phenylene-blue $C_{14}H_{16}N_4$·HCl. The dimethyl derivative of the preceding substance is formed either by the joint oxidation of dimethyl-*p*-phenylenediamine and *m*-phenylenediamine hydrochloride, or by mixing together lukewarm solutions of nitrosodimethylaniline hydrochloride and *m*-phenylenediamine, both dissolved in glacial acetic acid. It forms bronze-coloured crystals, readily soluble in water, with a purplish-blue shade. On the addition of mineral acids unstable diacid salts of a yellowish-brown colour are formed. The aqueous solution is decomposed by prolonged boiling, yielding neutral violet, a colouring matter of the eurhodine group (*v. Safranine*).

Literature.—Otto N. Witt, D. R. P. 15272, 1880; Eng. Pat. 4846, 1880.

Tolylene-blue $C_{15}H_{18}N_4$·HCl

Constitution



$$\begin{array}{l} N\begin{smallmatrix}CH_3\\ CH_3\end{smallmatrix}\cdot HCl \\ \;| \\ C_6H_4 \\ \;| \\ N \\ \;\| \\ H_2N-C_6H_2\cdot CH_3 \\ \;\| \\ NH \end{array}$$

This is the most thoroughly investigated member of the group. It is formed by the action of oxidising agents upon a mixture of dimethyl-*p*-phenylenediamine and *m*-tolylenediamine, or by the direct combination of nitrosodimethylaniline hydrochloride and free *m*-tolylenediamine. It is best prepared by the latter method. On mixing lukewarm aqueous solutions of the two ingredients in the proportion of equal molecules the blue is formed at once, and on cooling settles out in the shape of glistening bronze-coloured crystals which have the composition $C_{15}H_{18}N_4$·HCl. On adding hydrochloric acid to an aqueous solution of this compound a much more soluble diacid salt

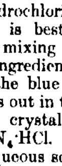
$$C_{15}H_{18}N_4\cdot HCl$$

of a reddish-brown colour, is formed. By the action of reducing agents, especially stannous chloride, the leuco derivative of tolylene-blue, dimethyltriaminotolylphenylamine $C_{15}H_{20}N_4$ is formed. An aqueous solution of the blue is decomposed by prolonged ebullition. The products of this decomposition are leucotolylene-blue and dimethyldiaminotoluphenazine (*Tolylene red, v.* AZINES).

Literature.—Otto N. Witt (Ber. 12, 931; Chem. Soc. Trans. 1879, 356; D. R. P. 15272, 1880; J. Soc. Chem. Ind. 1882, 256); R. Nietzki (Ber. 16, 1883, 475).

II. Indophenols.

The simplest *indophenol* $C_{12}H_{10}N_2O$



$$\begin{array}{c} O \\ \| \\ C_6H_4 \\ \| \\ N \\ | \\ C_6H_4 \\ | \\ NH_2 \end{array}$$

was prepared in 1880 and described by the inventors, Horace Köchlin and Otto N. Witt in their fundamental patents: D. R. P. 15915, Amer. Pat. 261518, Fr. Pat. 141843, Eng. Pat. 1373, 5249, 1881. It may be obtained by any of the processes indicated for the purpose by theory (see above, modes of formation). The best method for its preparation is the joint oxidation of *p*-phenylenediamine and phenol dissolved in water in equimolecular proportions with oxidising agents, which act in a neutral or alkaline solution, such as sodium ferricyanide, potassium persulphate, or hypochlorites. The last-named are exclusively used in industrial work. The dyestuff, which is of a reddish-blue shade, settles out at once. It is, however, very impure and contains other colouring matters which are formed by the condensation of part of the indophenol formed into more complicated indophenols of a higher molecular weight. According to the D. R. PP. 179294 and 179295, this is not the case if lead or manganese peroxides be used as an oxidising agent. Another method, indicated in the D. R. PP. 160710 and 168229 consists in oxidising a mixture of phenol with the monoacetyl or the monoaryl sulphonic derivatives of *p*-phenylenediamine and subsequent decomposition with alkali.

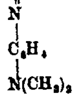
This dyestuff is insoluble in water, easily soluble in alcohol, ether, or benzene. Acids dissolve it readily with a yellow colour. The solution is quickly decomposed on standing.

A very similar dyestuff of a bluer shade may be obtained by the joint oxidation of a mixture of *p*-phenylenediamine and *p*-xylenol in molecular proportions.

Other nearly allied indophenols are prepared by the joint oxidation of *o*-tuluidine and *p*-aminophenol (Cassella and Co., D. R. P. 199963, 1901); and by the action of nitrosophenol upon *p*-chloro-*o*-nitrodiphenylamine (Kalle & Co., D. R. P. 205391, 1907).

All these indophenols are extremely similar in their properties. Notwithstanding the intensity and beauty of their blue coloration they have not acquired any importance as practical dyestuffs, probably because they are so easily attacked and decomposed by mineral acids. But in later years they have assumed great importance as raw materials for the manufacture of very fast blue sulphur dyes, and this has caused the appearance of numerous patents for the production of such indophenols, the more important of which only can be mentioned in this article.

Dimethyl derivative of simplest indophenol, $C_{14}H_{14}N_2O$,

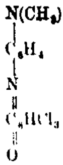


$$O = C_6H_4 = N - C_6H_4 - N(CH_3)_2$$

is obtained like the preceding compounds by joint oxidation from a mixture of phenol and dimethyl-*p*-phenylenediamine or by oxidising a mixture of dimethylaniline and *p*-aminophenol; it crystallises from alcohol in glistening green needles. Its alcoholic solution is of a brilliant greenish-blue colour.

Literature.—Horace Köchlin and Otto N. Witt, D. R. P. 15915, 1881. Leop. Cassella & Co., second addition to D. R. P. 15915.

Dimethyl-trichloroindophenol $C_{14}H_{11}Cl_3N_2O$



$$N(CH_3)_2 - C_6H_4 - N = C_6HCl_3 = O$$

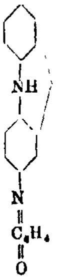
is obtained by mixing alcoholic solutions of trichloroquinonechloroimide (1 mol.) and dimethylaniline (2 mols.), according to the equation:

$$C_6HCl_3(NCl)O + 2C_6H_5 \cdot N(CH_3)_2 = C_{14}H_{11}Cl_3N_2O + C_6H_5N(CH_3)_2HC$$

Recrystallised from alcohol, it forms long green glistening needles, which have the general character of the indophenols and are comparatively stable. On reduction it yields the corresponding leuco compound, dimethylaminohydroxytrichlorodiphenylamine, $C_{14}H_{13}Cl_3N_2O$.

Literature.—Schmitt and Anderson (J. pr. Chem. [ii.] 24, 435).

Carbazole indophenol. This curious substance, which has been obtained by Cassella & Co. according to mode of formation No. 8 from carbazole and nitrosophenol has evidently the constitution:

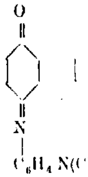


It is of great importance because on being heated with polysulphides it yields *hydron blue*, a sulphur dye insoluble in sodium sulphide solution, but capable of being used in the vat in exactly the same way as indigo and giving deep blue shades which are quite as fine and fast as those obtained with indigo itself. It is therefore expected to become a serious competitor of indigo blue. (*See* INDIGO, ARTIFICIAL, and INDIGOID DYESTUFFS; VAT DYES, MODERN.)

All the indophenols mentioned so far have this in common, that they are derivatives of *p*-quinone, and this accounts for the similarity of their properties and chemical behaviour.

A marked difference in this respect is shown by the indophenols which are derived from naphthaquinone which is itself less reactive and consequently more stable than the benzene derivative. This stability also shows itself in the naphthindophenols which can therefore claim to be applicable and even valuable dyestuffs.

Although a large number of these substances is foreseen by theory, the only well-known member of the group is the one first discovered, the *typical indophenol of commerce* $C_{18}H_{16}N_2O$ (vat blue, Küpenblau), the structure of which is expressed by the constitutional formula



It was discovered in 1880 by Horace Köchlin and Otto N. Witt and described in their fundamental indophenol patents already mentioned.

It is prepared from an alkaline mixture of dimethyl-*p*-phenylenediamine and α-naphthol in molecular proportions by oxidation. On a small scale potassium ferricyanide or ammonium persulphate is the most convenient oxidising agent, whilst on the manufacturing scale air is blown through the liquid, or a solution of sodium hypochlorite is employed. It may also be prepared by adding potassium chromate to the alkaline mixture of the ingredients and acidifying with acetic acid. Another process consists in simply heating on the water-bath an alcoholic solution of free nitrosodimethylaniline and sodium α-naphthoxide; or in bringing together, in an aqueous solution, α-naphthol, nitrosodimethylaniline, and caustic soda; this mixture is rapidly transformed into indophenol if a small quantity of a reducing agent, such as sodium stannite or glucose, be added.

Indophenol forms a dark-blue microcrystalline powder with a coppery metallic lustre, exactly resembling indigo. It is quite insoluble in water, sparingly soluble in spirit, ether, or benzene. It dissolves in dilute mineral acids, forming salts of a yellow colour, which are, however, quickly decomposed. In this decomposition α-naphthaquinone is formed as one of the products. Indophenol is slightly volatile; on being strongly heated it forms a sublimate resembling sublimed indigo. By reducing agents it is transformed into its leuco derivative

$$C_{18}H_{18}N_2O$$

dimethylaminophenylhydroxynaphthylamine. This has been an article of commerce under the name of indophenol-white. It is quite stable in an acid state, but in the presence of alkalis it rapidly absorbs the oxygen of the air, indophenol being regenerated.

The application of indophenol to dyeing and calico-printing is based either on the formation of the dyestuff on the fibre, or on the oxidation of its ready-formed leuco derivative after fixing the latter on the fibre. The first method is rarely employed. As an example the following description, taken from the patent specification, may serve: Bleached calico is printed with a thickened mixture of aminodimethylaniline and sodium α-naphthoxide; after drying and steaming it is passed through a solution of potassium dichromate, when the blue is instantaneously developed. As a rule ready-formed indophenol is employed for printing, reduced by being mixed with a solution of stanneus acetate, then thickened with starch paste and printed on the fibre. The colour is developed by steaming and exposure to the air. Indophenol-blue on calico is very fast to the action of soap, fairly so to the action of light, but rather susceptible to acids.

In spite of its many good qualities, indophenol at first did not meet with an enthusiastic reception in the tinctorial world. This was changed by an interesting and for its time (about 1885–1895) important discovery of the Swiss manufacturing firm L. Durand, Huguenin & Co. It is based on the fact that indophenol, mixed with indigo, assumes the properties of the latter and may consequently be used in the vat process, especially with hydrosulphite as a reducing agent.

It is more than probable that the two leuco compounds of indigo and indophenol are capable of combining chemically and that the resulting substance is endowed with strong affinities for the fibre, especially cotton. It is thus easily taken up from the vat and, on being reoxidised on the fibre, deposits in the molecular interstices of the latter an intimate mixture or even a chemical combination of the two dyestuffs, indigo and indophenol.

An intimate mixture of indigo and indophenol, ground together into an impalpable powder is the 'vat blue' or 'kupenblau' of commerce, which may still occasionally be met with, although it has lost many of its advantages by the great reduction in the price of indigo and by the introduction of the cheap and excellent dark-blue sulphur dyes, many of which are also capable of being applied in the vat.

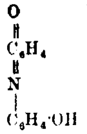
Literature.—Otto N. Witt and Horace Köchlin, D. R. P. 15915, 1881, with several additions; and corresponding patents in England, France, the United States, Sweden, Belgium, and Austria; Otto N. Witt, J. Soc. Chem. Ind. 1882, 144, 225, 405; R. Möhlau, Ber. 16, 2845.

III. ACID INDOPHENOLS.

It has already been mentioned that these substances are not true acids, containing no carboxyl groups in their molecule. They owe their name to the fact that, containing no amino and several hydroxyl groups, they readily combine and form stable salts with metallic oxides. Of these only the alkali salts are known. In a solid state they form crystalline powders with a green or copper-coloured metallic lustre. They are easily soluble in water with an intense blue coloration. By the addition of acids the free indophenols are deposited in the shape of brown or reddish flakes, which are soluble with a dark-red colour in spirit, ether, benzene, and analogous solvents.

The acid indophenols show in even a higher degree the tendency of the whole group to polymerise into colouring matters of a more complex molecule. It is therefore extremely difficult to prepare them in a state of purity. On the other hand, they do not show the susceptibility to acids so characteristic of the indamines and typical indophenols. It is therefore possible to prepare them not only in alkaline but also in acid solutions and by means of oxidising agents* which act in such. Their modes of formation are given above under methods 4, 6, 7, 12, and 15.

Typical acid indophenol $C_{12}H_9NO_2$,

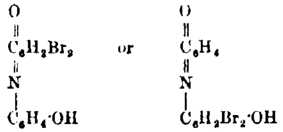


$O{=}C_6H_4{=}N{-}C_6H_4{\cdot}OH$

The possibility of preparing this compound by the joint oxidation of *p*-aminophenol and phenol is mentioned in Koechlin and Witt's fundamental indophenol patents, but its manufacture seemed at first to offer no interest. It is formed if quinoneimide is brought into contact with phenol, and R. Hirsch observed it on adding caustic potash to a solution of quinonechloroimide in phenol, but did not succeed in isolating it (Ber. 13, 1909). The cause of these difficulties was revealed by the D. R. P. 157288 of the Actiengesellschaft für Anilinfabrikation of Berlin. The formation of the dyestuff must take place at unusually low temperatures if its tendency for polymerisation in a nascent state is to be overcome. According to this patent, the product may be prepared with a good yield if an equimolecular mixture of phenol and *p*-aminophenol be oxidised with sodium hypochlorite at a temperature of −15° to −18°, preferably in solutions saturated with sodium chloride so that the sodium salt of the dyestuff is at once salted out of the liquid. It is thus obtained in the shape of glistening metallic green needles.

These dyestuffs become more stable and are therefore more easily prepared if their molecule be weighted by the introduction of various substituents :

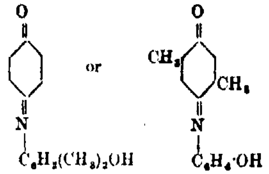
Acid dibromoindophenol $C_{12}H_7Br_2NO_2$,



$O{=}C_6H_2Br_2{=}N{-}C_6H_4{\cdot}OH$ or $O{=}C_6H_4{=}N{-}C_6H_2Br_2{\cdot}OH$

(See remarks on migration under 2 and 5.) has been prepared in various ways by R. Möhlau (Ber. 16, 2843). It may be obtained either by the joint oxidation of a mixture of dibromoaminophenol and phenol in molecular proportions, or by adding dibromo-quinonechloroimide, suspended in alcohol, to an alkaline solution of phenol. The sodium salt of the indophenol separates out in green glistening needles, which are soluble in water and alcohol with a pure blue colour. On adding acetic acid to the solution the free indophenol settles out in dark-red, almost black prisms with a metallic lustre. It is soluble in alcohol with a magenta colour. Mineral acids decompose this compound into dibromo-aminophenol and *p*-quinone. If a current of sulphur dioxide be introduced into the solution of the sodium indophenolate, the corresponding leuco compound $C_{12}H_9Br_2NO_2$, dihydroxydibromodiphenylamine, is formed. It crystallises in white glistening needles, melting at 170°.

Acid dimethylindophenol $C_{14}H_{13}NO_2$,



is also much more stable and therefore more easily prepared than the typical acid indophenol. This was shown in 1902 by L. Cassella & Co. in their D. R. P. 191863 and the corresponding Eng. Pat. 4653, 1902; 2617, 1902. According to these patents, 1 : 4 : 5-(*p*-) xylenol and *p*-aminophenol give a good yield of this dyestuff if subjected to joint oxydation in equimolecular proportions.

All these acid indophenols have assumed a new interest and are being largely investigated, since it has been shown that they are valuable raw materials for the manufacture of the sulphur dyes which have come so much to the front in these later years. O. N. W.

INDANE *v.* INDENE.

INDANTHRENE. Within recent years, considerable advances have been made in the discovery and commercial production of certain compounds belonging to the class of the vat dyes. By the term 'vat dye' is understood an insoluble pigment which, when reduced by an alkaline reducing agent, passes into a hydro-derivative soluble in the alkaline reducing solution. The hydro-derivative is absorbed by fabrics steeped in this solution and is then reconverted into the pigment when the material is exposed to the oxidising action of the air. Indigo, the most important of all colouring matters, is a typical vat dye, and it is apparent that the process entailed by the use of these colours not only produces the shades fastest to light and washing, but is also one of the simplest with which the dyer has to deal.

For many years research on the formation of new vat dyes was confined to the indigo group, but in the year 1901 it was demonstrated by R. Bohn that certain derivatives of anthraquinone could be applied for this purpose. The vat dyes of this series possess, however, one important property which distinguishes them from all other members of the class, that is, the vat formed by the alkaline reduction of the pigment is always strongly coloured. The hydro-derivatives are, therefore, themselves coloured substances, whereas the hydro-derivatives from other vat dyes, for example indigo-white, are colourless or at most faintly yellow.

The vat dyes of the indanthrene series may be conveniently divided into five groups :—

(1) Indanthrene.
(2) Flavanthrene.
(3) Benzanthrone colours.
(4) Anthraquinoneimide colours.
(5) Acyl derivatives of amindanthraquinone.

Indanthrene : *Preparation* (R. Bohn, D. R. P. 129845; Zusatze, 129846, 129847, 129848, 135407, 135408, 138167, 155485, 210223, and 216891; Scholl and Berblinger, Ber. 1903, 36, 3427).

The colouring matter is prepared by fusing β-aminoanthraquinone with caustic potash at 200°–300° and is found in the melt as the soluble potassium salt of the blue hydro-derivative of indanthrene which, when dissolved in water with free access of air, is converted into the insoluble blue colouring matter. At a lower temperature (150°–200°) alizarin is formed at the same time as indanthrene, but at the higher temperature this is transformed into a brown substance soluble in alkali; the separation of the blue colouring matter is, therefore, simple owing to its insolubility in the alkaline liquid. Whether produced at the higher or lower temperature, the indanthrene is not a homogeneous substance but consists of two compounds, indanthrene A and indanthrene B, the latter being worthless as a colouring matter. It is possible so to regulate the conditions as to cause indanthrene A to be the chief product; thus, when the fusion is carried out in the presence of potassium nitrate the product consists almost entirely of indanthrene A, and indanthrene B is only formed in small amount. By fusing β-aminoanthraquinone with caustic potash at a still higher temperature, that is at 330°–350°, the product is a yellow vat dye, flavanthrene (*v. infra*).

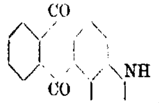
500 grams of caustic potash together with a little water are placed in a nickel basin which is heated by means of an anthracene bath. The melt is then heated to 200° and mixed with 20 grams of potassium nitrate; 100 grams of β-aminoanthraquinone are now gradually added with constant stirring. The temperature is raised to 250° and maintained at this point for half an hour when the melt is poured into water, the solution boiled, and the precipitated colour filtered and washed. The small quantity of indanthrene B present in the product is separated by taking advantage of the greater solubility of its hydro-derivative in dilute alkali. 100 grams of the crude indanthrene in the form of paste are diluted with 10 litres of water and warmed to 60°–70°; 200 grams of a 25 p.c. caustic soda solution and 1500 grams of sodium hydrosulphite solution (sp.gr. 1·074) are then added and the temperature of the mixture maintained at 60°–70° for 1 hour. By this time the colour will have completely dissolved, and the solution, when cooled, will slowly deposit the sodium salt of the hydro-derivative of indanthrene A as well-defined glistening needles with marked copper reflex. The salt is collected by filtration, washed with a little dilute caustic soda solution to which a small quantity of hydrosulphite solution has been added, and is then converted into pure indanthrene A by dissolving in hot water and allowing free access of air. The brown-red mother liquor contains the more soluble salt of the hydro-derivative of indanthrene B from which the colour separates as bluish-green flocks when air is led into the solution.

Indanthrene prepared in this manner is a dark blue powder with strong metallic reflex, and is practically insoluble in all the usual solvents. It dissolves with great difficulty in boiling aniline and in nitrobenzene, in the latter case to the extent of one part in 5000, forming a greenish-blue solution. It dissolves to the extent of 1 part in 500 in boiling quinoline, forming a blue solution from which the colour separates as characteristic curved needles resembling pure indigo in appearance; the solutions are without fluorescence. When heated it partly sublimes in the form of its characteristic needles and then decomposes with charring between 470° and 500°.

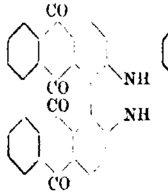
Constitution of indanthrene (Scholl, Ber. 1903, 36, 3410). Indanthrene as shown by its elementary analysis and molecular weight determination by the ebullioscopic method in quinoline has the molecular formula $C_{28}H_{14}O_4N_2$, and is therefore formed by the condensation of two molecules of β-aminoanthraquinone with loss of 4 atoms of hydrogen.

$$2C_{14}H_9O_2N - 4H \rightarrow C_{28}H_{14}O_4N_2$$

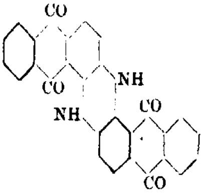
That these 4 hydrogen atoms are not removed from the amino-groups alone—in other words, that an azo compound is not formed—is shown by the fact that indanthrene when reduced does not yield β-aminoanthraquinone or a reduction product of this base. Moreover, as indanthrene no longer contains a free amino-group, it is probable that two of these hydrogen atoms are supplied by the two amino-groups and that the other two belong to the rings bearing the amino-groups in the two molecules of β-aminoanthraquinone taking part in the reaction. From the fact that 1 : 2-dihydroxyanthraquinone (alizarin) is always a product of the fusion in its earlier stages, it is reasonable to assume that the hydrogen atoms removed from the two rings are those in the ortho-position to the two amino-groups. This leads to two formulæ for indanthrene, namely—



β-Aminoanthraquinone residue.



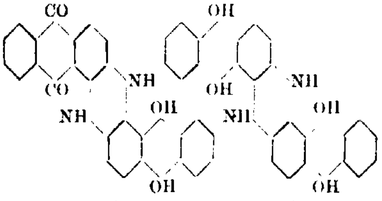
(1)



(2)

Since indanthrene is not reduced to a diamine, which would be the case if it possessed an ortho-diazine formula represented by (1), it follows that it must be a dihydroparadiazine represented by formula (2), or in other words, that it is *N*-dihydro-1 : 2 : 2′ : 1′-anthraquinoneazine. This view of the structure of indanthrene is completely upheld by its chemical behaviour. It has been suggested by Nietzki (Chemie der Organ. Farbstoffe, 5 Aufl. S. 121, 1906) that the formation of indanthrene is due to the intermediate production of 1-hydroxy-2-aminoanthrahydroquinone, two molecules of which combine to form tetrahydroindanthrene. This has, however, been disproved by Scholl, Berblinger, and Mansfield (Ber. 1907, 40, 320), who find that neither 1-hydroxy-2-aminoanthrahydroquinone nor 1-hydroxy-2-aminoanthraquinone yields indanthrene when fused with potash.

Properties of indanthrene.—When indanthrene in dilute alkaline solution is heated at 40°–50° with sodium hydrosulphite, it passes into a blue hydro-derivative, dihydroindanthrene. This substance possesses the property of dyeing unmordanted cotton blue, and when the fibre so dyed is exposed to the oxidising action of the air the hydro-derivative is reconverted into indanthrene. When indanthrene is reduced by zinc dust, a brown hydro-derivative is formed; this hydro-derivative is also converted into indanthrene on exposure to the air. Scholl, Steinkopf, and Kabacznik (Ber. 1907, 40, 390) have shown that the blue substance is *N*-dihydro-1 : 2 : 2′ : 1′-anthraquinone-anthrahydroquinoneazine (1), and that the brown solution contains *N*-dihydro-1 : 2 : 2′ : 1′-anthrahydroquinoneazine (2).

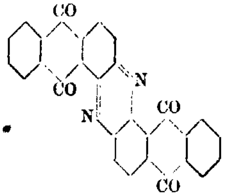


(1) Blue hydro-derivative.

(2) Brown hydro-derivative.

The compound commercially known as indanthrene S is the disodium salt of formula 2, and this is the substance which is always formed in the indanthrene vat.

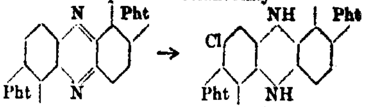
When indanthrene is oxidised by nitric acid (sp.gr. 1·24), it is converted into the yellow 1 : 2 : 2′ : 1′-anthraquinoneazine (Scholl and Berblinger, Ber. 1903, 36, 3427; *cp.* Scholl, Berblinger, and Mansfield, *ibid.* 1907, 40, 321).



This substance is reconverted into indanthrene on reduction, a reaction which may be effected by means of direct sunlight.

Indanthrene is one of the most stable substances known; sodium hypochlorite, which destroys most colouring matters such as the alizarins, indigos, &c., merely converts indanthrene into the above yellow azine, which can be readily reconverted into indanthrene by means of sodium hydrosulphite.

When halogen atoms enter the molecule of indanthrene, the shade becomes greener. Indanthrene blue GC (D. R. P. 138167) is a bromindanthrene; indanthrene blue GCD and CE are chloro-derivatives (D. R. P. 155415). Monochlorindanthrene is prepared by the action of boiling concentrated hydrochloric acid on anthraquinoneazine whereby chlorination and reduction take place simultaneously—



$$\text{Pht} = \text{Phthaloyl } C_6H_4{<}^{CO}_{CO}$$

The reaction is analogous to the formation of chlorhydroquinone from quinone and hydrochloric acid. Owing to the alkali required in the preparation of the indanthrene vat, this substance cannot be used for the dyeing of wool. The sulphonic acid (D. R. P. 216891) can be employed, however, for this purpose. The blue produced on cotton by the aid of indanthrene is one of the fastest known. (For the method of dyeing *cp.* D. R. P. 139834; for printing, *cp.* D. R. PP. 132402, 140573.)

Flavanthrene (indanthrene yellow, chloranthrene yellow). As already mentioned, flavanthrene was discovered by R. Bohn (D. R. P. 138119), in the products formed by the fusion of β-aminoanthraquinone with potash. At the present time it is prepared by treating β-aminoanthraquinone with antimony pentachloride in boiling nitrobenzene. (*V.* art. FLAVANTHRENE.)

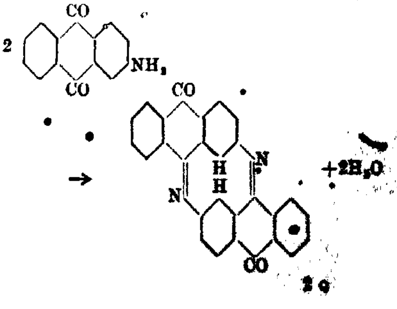
When reduced by alkaline hydrosulphite, flavanthrene yields a violet-blue vat in which cotton is dyed a deep blue; when exposed to the oxidising action of the air the colour changes, in the course of a few minutes, to the light yellow of flavanthrene.

Preparation.—Ten grams of β-aminoanthraquinone are gradually added to a solution of 35 grams anhydrous antimony pentachloride in 100 grams nitrobenzene, heated at 60°–80°. The mixture is then heated to the boiling-point and maintained at this temperature for one hour, the containing flask being without a condenser. The yellow-brown solution deposits, on cooling, chemically pure flavanthrene as brownish-yellow needles.

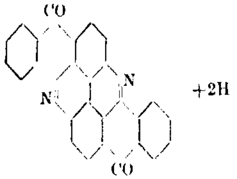
The constitution of flavanthrene has been determined by Scholl (Ber. 1907, 40, 1691). The molecular formula is $C_{28}H_{12}O_2N_2$, and it must therefore be formed from β-aminoanthraquinone in accordance with the equation

$$2C_{14}H_9O_2N \rightarrow C_{28}H_{12}O_2N_2 + 2H + 2H_2O$$

The two molecules of water formed in the reaction at once suggest the interaction of the hydrogen atoms of the amino-groups with the carbonyl oxygens, an assumption which leads to the following formula:—

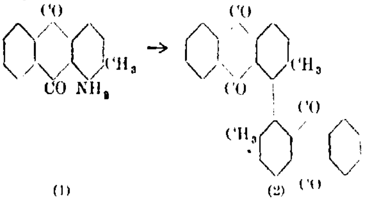


The ring then closes thus :



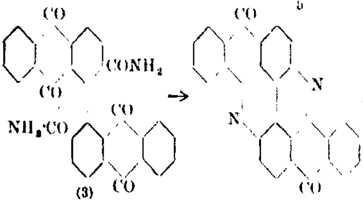
The hydrogen thus formed is not eliminated in the free condition, but reduces the colour to the dihydro-base, the state in which it always occurs in the melt.

This view of the constitution of flavanthrene has been confirmed by Scholl by the actual synthesis of this substance in the following way : 2-methyl-1-aminoanthraquinone (1) is converted into 2 . 2′-dimethyl-1 1′-dianthraquinonyl (2) either by heating the corresponding iodide with copper powder or by the action of copper powder and acetic anhydride on the diazonium sulphate :



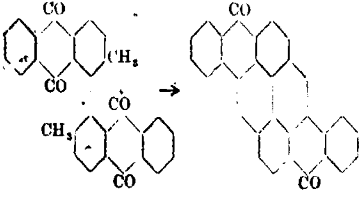
(1) (2)

This substance is then oxidised to the dicarboxylic acid which is converted, through the acid chloride, into the acid amide (3) An attempt to prepare the amino-compound from this by the action of bromine and potash led to the formation of flavanthrene .



(3)

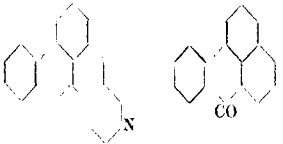
Pyranthrene (indanthrene golden orange) (D. R. P. 175067 ; Ber. 1910, 43, 346 ; 1911, 44, 1448 ; R. Scholl). This substance is a valuable orange vat dye which is formed by the elimination of two molecules of water from 2 : 2′-dimethyl-1 : 1′-dianthraquinonyl (formula (2) above). It differs from flavanthrene in having two methin groups in place of the azino nitrogen atoms :



The condensation proceeds readily in the presence of a dehydrating agent such as zinc chloride or by merely heating alone at 350°–380°. Pyranthrene forms a magenta red vat with alkaline hydrosulphite in which cotton is dyed a deep red ; on exposure to the air this oxidises to a fast orange.

The entrance of halogen atoms into the molecule of pyranthrene reddens the shade and of these derivatives dibromopyranthrene (D. R. P. 218162) is the most red.

The benzanthrone colours. The vat colours of this class were discovered by O. Bally (Ber. 1905, 398, 14 ; D. R. P. 176018), who found that when the Skraup quinoline synthesis was applied to 2-aminoanthraquinone, two glycerol residues entered into the molecule, forming benzanthronquinoline (1) :



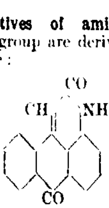
(1) (2)

When this reaction was applied to anthraquinone, benzanthrone (2) was formed.

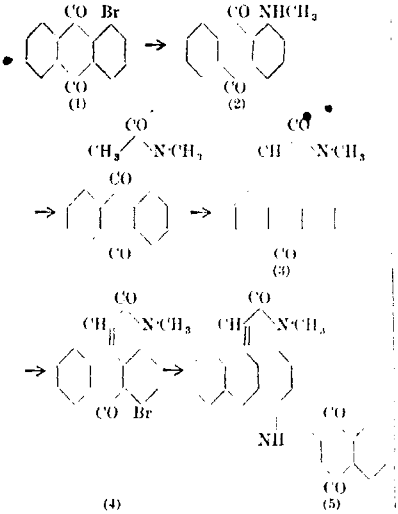
Blue vat dyes are formed from these substances on fusion with potash, two molecules condensing with loss of four atoms of hydrogen. To this group belong indanthrene dark blue (D. R. P 185221), which is a mixture of indanthrene blue BO and indanthrene violet RT (Chem. Zeit 1917, 41, 713), as well as its isomeride and chlorine substitution product, indanthrene violet (D. R. PP. 177574, 194252, 217570) ; indanthrene green (D. R. P. 185222) is an amino-derivative of indanthrene dark blue ; if the last-named colour is strongly chlorinated a deep, very fast black is formed. Cyananthrene and violanthrene (Annalen, 1913, 398, 82) also belong to this group.

Colours derived from anthraquinoneimide. These colours consist of several anthraquinone residues joined together in much the same manner as in flavanthrene. They are, for the most part, trianthraquinonediimides and their substitution products which are formed by the condensation of aminoanthraquinones and halogenanthraquinones. Indanthrene Bordeaux (D. R. PP. 184905 and 206177) and indanthrene red (D. R. P. 197554) belong to this group.

Acyl derivatives of aminoanthraquinone. Colours of this group are derived from anthraquinonepyridone : by the replacement of the hydrogen atom in the para-position to the imino-group by arylamino residues. Thus algol red is formed when 1-bromanthraquinone (1) is converted into methyl-1-aminoanthraquinone (2) by means of



methylamine. This is acetylated and condensed to *N*-methylanthraquinonepyridine (3), which is then brominated, yielding 4-brom-*N*-methylanthraquinonepyridine (4), and this, on condensation with 2-aminoanthraquinone, yields algol red (5):

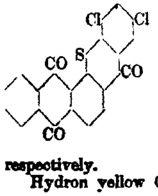


(1) (2) (3) (4) (5)

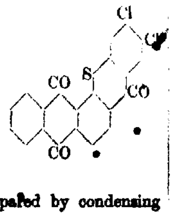
Other members of this class are algol yellow, algol rose, algol scarlet, algol green, algol blue, and algol brown. They all yield coloured vats with sodium hydrosulphite in which cotton is dyed the colour of the dihydro-derivative; on exposure to the air the colour on the fibre is quickly oxidised to the algol dye.

The following indanthrene colours are formed from anthraquinone derivatives by the aid of various reactions, but have not as yet had a definite constitution assigned to them. Indanthrene maroon (D. R. P. 160184) and indanthrene grey (D. R. P. 157685) are derived from diaminoanthraquinones. Indanthrene orange and indanthrene copper (D. R. P. 198048) are prepared from the acetyl derivatives of aminoanthraquinone by means of phosphorus oxychloride. Cibanon yellow, cibanon orange, and cibanon brown, are derived from methylanthraquinone and its derivatives.

Indanthrene yellow GN and indanthrene gold orange GN (U.S. Pats. 1044673, 1044674, 1044675) have the formula:

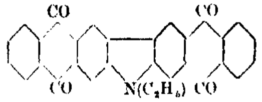


and



respectively.

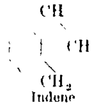
Hydron yellow G, prepared by condensing *N*-ethylcarbazole with phthalic anhydride (Eng. Pat. 2887411) has the formula:



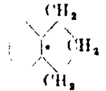
J. F. T.

INDAZINE *v.* Azines.

INDENE. The compounds of the indene group are derived from the hydrocarbons indene and hydrindene



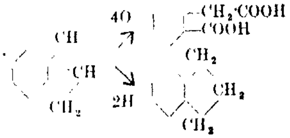
Indene



Hydrindene.

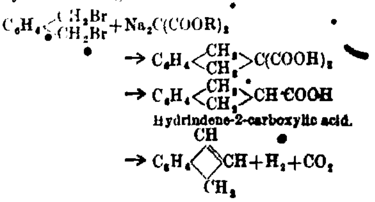
by the replacement of the hydrogen atoms either in the five-membered ring or in the aromatic nucleus. They therefore yield two classes of derivatives: (1) Those of aromatic character which are formed when the hydrogen atoms of the benzene ring are substituted. (2) Those of aliphatic character which are produced by the replacement of the hydrogen atoms attached to the five-membered ring.

Constitution.—The constitution of indene follows from its conversion into homophthalic acid by oxidation with permanganate:



and the structure of hydrindene is shown by the production of this substance from indene by reduction with sodium and alcohol.

Occurrence and preparation of indene and indene derivatives. Indene was isolated from coal-tar by Kramer and Spilker (Ber. 1890, 23, 3276), who obtained it from the higher boiling fraction of the light oil in which it occurs to the extent of about 30 p.c. It is formed, accompanied by hydrindene, in the dry distillation of paraindene $(C_9H_8)x$, a white substance which is formed when benzene containing indene is treated with concentrated sulphuric acid (Ber. 1900, 33, 2261). It has, moreover, been prepared synthetically by Perkin and Revay (Chem. Soc. Trans. 1894, 65, 228; *cp.* Kipping and Hall, *ibid.* 1900, 77, 469), by the distillation of barium hydrindenecarboxylate, a substance which can be prepared from *o*-xylylene dibromide by the following series of reactions.



$$C_6H_4{<}\begin{matrix}CH_2Br\\CH_2Br\end{matrix}+Na_2C(COOR)_2$$

$$\rightarrow C_6H_4{<}\begin{matrix}CH_2\\CH_2\end{matrix}{>}C(COOH)_2$$

$$\rightarrow C_6H_4{<}\begin{matrix}CH_2\\CH_2\end{matrix}{>}CH{\cdot}COOH$$

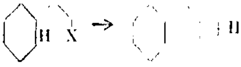
Hydrindene-2-carboxylic acid.

$$\rightarrow C_6H_4{<}\begin{matrix}CH\\CH_2\end{matrix}{>}CH+H_2+CO_2$$

Owing to the ease with which the five-membered ring is usually formed, derivatives of indene and of hydrindene are readily produced from the corresponding benzene derivatives, having a side chain containing the requisite number of carbon atoms. The benzene derivatives which lend themselves to this change may therefore be divided into two classes: (1) those having one side chain of three carbon atoms; (2) those having two side chains, attached in the ortho-position to the benzene nucleus, one of these side chains being composed of one carbon atom, the other of two carbon atoms.

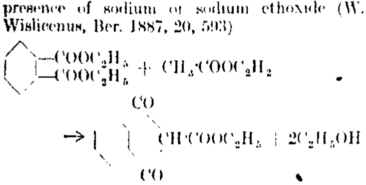
The derivatives of hydrocinnamic acid fall within the first class and a large number of indene compounds have been prepared from this substance and its derivatives (*v.* Miller and Rohde, Ber. 1902, 35, 1762).

The general character of this reaction may be expressed by the scheme

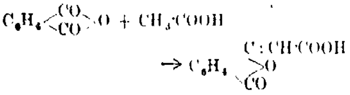


(X = halogen).

As an illustration of the formation of hydrindene derivatives by the method indicated under class (2), the formation of 1 : 3-diketohydrindene can be given. The ethyl salt of the carboxylic acid of this substance is formed when ethyl phthalate is condensed with ethyl acetate in the presence of sodium or sodium ethoxide (W. Wislicenus, Ber. 1887, 20, 593)

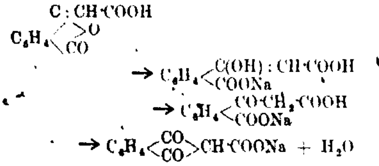


A curious molecular rearrangement, leading to the formation of hydrindene derivatives, has been discovered by Gabriel and Neumann (Ber. 1893, 26, 951). The condensation of phthalic anhydride and sodium acetate in the presence of acetic anhydride leads to the formation of phthalylacetic acid:



$$C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}O + CH_3{\cdot}COOH \rightarrow C_6H_4\begin{matrix}C:CH{\cdot}COOH\\ \quad{>}O\\CO\end{matrix}$$

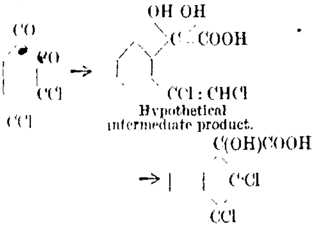
and this substance, when treated with sodium methoxide, passes into a derivative of 1 : 3-diketohydrindene. The reaction may be explained as follows:—



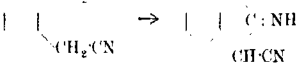
$$C_6H_4\begin{matrix}C:CH{\cdot}COOH\\ \quad{>}O\\CO\end{matrix} \rightarrow C_6H_4{<}\begin{matrix}C(OH):CH{\cdot}COOH\\COONa\end{matrix} \rightarrow C_6H_4{<}\begin{matrix}CO{\cdot}CH_2{\cdot}COOH\\COONa\end{matrix} \rightarrow C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}CH{\cdot}COONa + H_2O$$

It can be applied to the preparation of numerous derivatives of 1 : 3-diketohydrindene.

The formation of indene derivatives from compounds containing the naphthalene nucleus in which the stability of the ring is weakened by the presence of strongly negative groups has been investigated by Zincke and his pupils (Ber. 1886, 19, 2500; 1887, 20, 1265, 2894, 3216; 1888, 21, 491, 2381, 2379; 1894, 27, 744; Annalen, 1892, 267, 319; 1894, 283, 341; 1898, 300, 197). This type of reaction may be illustrated by the transformation of dichloro-β-naphthaquinone into dichlorohydroxyindene carboxylic acid by the action of caustic alkali.



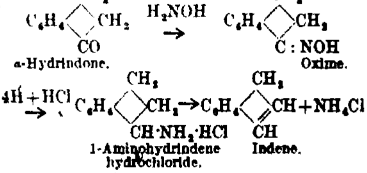
Derivatives of hydrindene can also be formed from ortho-benzenoid dinitriles. Thus *o*-phenylenediacetonitrile passes into β-imino-α-cyanohydrindene when its solution in alcohol, containing a trace of sodium ethoxide, is warmed (Moore and Thorpe, Chem. Soc. Trans. 1908, 93, 165).



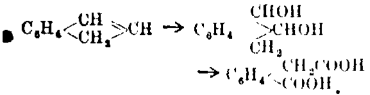
Preparation of indene from coal-tar. The fraction boiling at 176°–182° obtained from crude benzene is first titrated with bromine and the amount of unsaturated material present determined. A sufficient quantity of picric acid is then added to the hot liquid and the crystalline material which separates is isolated by filtration. The impure picrate is then distilled with steam, under which conditions the naphthalene picrate contained in it is only slowly decomposed, whereas the indene picrate is readily transformed into indene which passes over with the steam. The crude hydrocarbon is then again converted into the picrate and the operation repeated until pure indene is obtained. Indene picrate forms golden yellow needles which melt at 98°.

Indene is a clear mobile liquid boiling at 179·5°–180·5° (corr.).

It is obtained pure only with great difficulty, as it rapidly absorbs oxygen from the air and when kept in a sealed vessel polymerises to a resin. The most convenient synthetic method for the preparation of indene is from α-hydrindone, the oxime of which passes on reduction into 1-aminohydrindene, and when the hydrochloride of this base is distilled, ammonium chloride and indene are formed, thus—

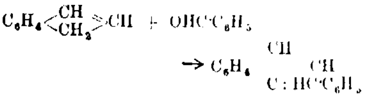


Reactions of indene. Indene readily combines with bromine, forming 1 : 2-dibromohydrindene $C_6H_4<\substack{CH_2\\CHBr}>CHBr$ and when oxidised passes first into hydrindene glycol and then into homophthalic acid



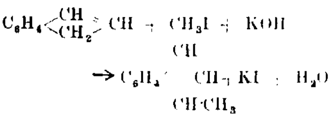
$$C_6H_4<\substack{CH\\CH_2}>CH \rightarrow C_6H_4\substack{CHOH\\>CHOH\\CH_2} \rightarrow C_6H_4<\substack{CH_2COOH\\COOH}.$$

The hydrogen atoms of the methylene group present in indene are reactive; thus, when the hydrocarbon is condensed with benzaldehyde, benzylidene indene is formed:



$$C_6H_4<\substack{CH\\CH_2}>CH + OHC\cdot C_6H_5 \rightarrow C_6H_4\substack{CH\\ \quad CH\\C:HC\cdot C_6H_5}$$

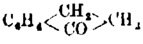
In fact, this grouping behaves in much the same manner as the corresponding complex in ethyl malonate and analogous compounds, thus, when indene is treated with methyl iodide and powdered alkali, methylindene is formed (Marckwald, Ber. 1900, 33, 1504):



$$C_6H_4<\substack{CH\\CH_2}>CH + CH_3I + KOH \rightarrow C_6H_4\substack{CH\\ \quad CH\\CH\cdot CH_3} + KI + H_2O$$

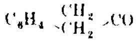
Hydrindene (Indane) $C_6H_4<\substack{CH_2\\CH_2}>CH_2$ This hydrocarbon can be prepared by dissolving 1 part of indene in 10 parts of 90 p.c. alcohol and adding metallic sodium in small proportions until the product is no longer converted into a resin by concentrated sulphuric acid. It is a mobile oil boiling at 176°–176·5° (corr.).

The ketones derived from hydrindene. The ketones derived from this substance may be classified as follows: (1) The mono-ketones (hydrindones), which comprise.



$$C_6H_4<\substack{CH_2\\CO}>CH_2$$

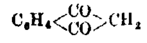
α-Hydrindone.



$$C_6H_4<\substack{CH_2\\CH_2}>CO$$

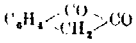
β-Hydrindone.

(2) **The di-ketones** (di-ketohydrindenes), which are



$$C_6H_4<\substack{CO\\CO}>CH_2$$

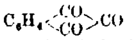
1 : 3-Diketohydrindene.



$$C_6H_4<\substack{CO\\CH_2}>CO$$

1 : 2-Diketohydrindine.[1]

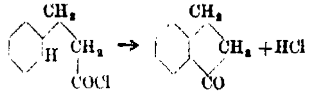
(3) The tri-ketone is



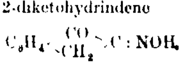
$$C_6H_4<\substack{CO\\CO}>CO$$

1 : 2 : 3-Triketohydrindene.

α-Hydrindone $C_6H_4<\substack{CH_2\\CO}>CH_2$. This substance is best prepared by the action of aluminium chloride on the chloride of hydrocinnamic acid in accordance with the following equation:—

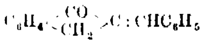


It forms rhombic plates from dilute alcohol, melts at 40° and boils at 243°–245°. The oxime melts at 146° and the phenyl hydrazone at 130°–131°. The methylene group adjacent to the carbonyl group in α-hydrindone is reactive and derivatives of the ketone can be formed by the usual reagents. Thus amyl nitrite gives the oxime of 1 : 2-diketohydrindene



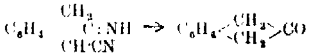
$$C_6H_4<\substack{CO\\CH_2}>C:NOH,$$

and the action of benzaldehyde leads to the formation of the benzylidene derivative



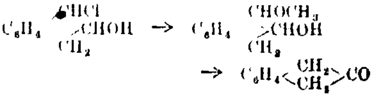
$$C_6H_4<\substack{CO\\CH_2}>C:CHC_6H_5$$

β Hydrindone $C_6H_4<\substack{CH_2\\CH_2}>CO$. This ketone is best prepared from β-imino-α-cyanohydrindene by distilling with dilute sulphuric acid (Moore and Thorpe, Chem. Soc. Trans. 1908, 93; *cf.* also Chem. Soc. Proc. 1911, 27, 128).



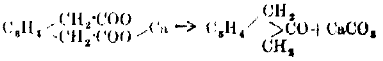
$$C_6H_4\substack{CH_2\\ \quad C:NH\\CH\cdot CN} \rightarrow C_6H_4<\substack{CH_2\\CH_2}>CO$$

It can also be prepared from the indene of coal-tar (Heusler and Schieffer, Ber. 1899, 32, 28). The method most convenient for this purpose is to convert indene into the *chlorohydrin* by the method of Kramer and Spilker (Ber. 1890, 23, 3280) and then to transform this into the methoxy derivative which, with dilute sulphuric acid, yields β-hydrindone:



$$C_6H_4\substack{CHCl\\>CHOH\\CH_2} \rightarrow C_6H_4\substack{CHOCH_3\\>CHOH\\CH_2} \rightarrow C_6H_4<\substack{CH_2\\CH_2}>CO$$

It can also be formed by distilling the calcium salt of o-phenylenediacetic acid (Benedikt, Annalen, 1893, 275, 353; Schad, Ber. 1893, 26, 222):



$$C_6H_4<\substack{CH_2\cdot COO\\CH_2\cdot COO}>Ca \rightarrow C_6H_4<\substack{CH_2\\CH_2}>CO + CaCO_3$$

β-Hydrindone crystallises from dilute alcohol as long needles, melts at 61° and boils with partial decomposition at 220°–225°. The oxime melts at 155°, the phenylhydrazone at 120° and the semi-carbazone at 210°.

1 : 3 Diketohydrindene $C_6H_4<\substack{CO\\CO}>CH_2$, is probably the best known derivative of indene and is formed by the method of W. Wislicenus already described. It may be isolated (Kaufmann, Ber. 1897, 30, 385) by dissolving the sodium compound of ethyl diketohydrindenecarboxylate, prepared from ethyl phthalate and ethyl acetate, in as little boiling water as possible, cooling to 70°–75° and adding dilute sulphuric acid. A vigorous evolution of carbon dioxide then ensues and the diketone separates in the crystalline form. 1 : 3-Diketohydrindene melts and decomposes at 129°–131°.

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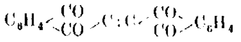
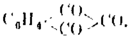
[1] This substance has been prepared by Perkin, Roberts and Robinson (Chem. Soc. Trans. 1912, 101, 232) from isonitroso-α-hydrindone (Kipping, *ibid.* 1894, 65, 492). It crystallises from benzene as golden-yellow plates, m.p. 95°–115°, and gives a semicarbazone (m.p. 230°–233° with decomposition), an osazone (m.p. 230°–235°), and an indenoquinoxaline (m.p. 164°–165°).

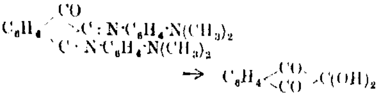
As is to be expected, the methylene group between the two carbonyl complexes of 1 : 3-diketohydrindene is exceedingly reactive and this substance shows all the reactions of the β-diketones. When oxidised by hydrogen peroxide or potassium persulphate, it is converted into the oxygen analogue of indigo, having the formula



$$C_6H_4<\substack{CO\\CO}>C:C<\substack{CO\\CO}>C_6H_4$$

This substance crystallises from aniline as glistening red needles.

1 : 2 : 3-Triketohydrindene  $C_6H_4<\substack{CO\\CO}>CO.$ A substance of this formula was prepared in small quantity by Kaufmann (Ber. 1897, 30, 387) by the oxidation of 1 : 3-diketohydrindene with hydrogen peroxide. The compound prepared in this way crystallised from glacial acetic acid as brown leaflets which melted and decomposed at 190°–206°. It is probable that the substance obtained by Kaufmann possesses another structure, and that the true triketohydrindene is the compound prepared by Ruhemann, in the form of a hydrate, by the action of dilute sulphuric acid on the compound formed by the condensation of α-hydrindone with p-nitrosodimethylaniline



$$C_6H_4<\substack{CO\\C{\cdot}N{\cdot}C_6H_4{\cdot}N(CH_3)_2}>C:N{\cdot}C_6H_4{\cdot}N(CH_3)_2 \rightarrow C_6H_4<\substack{CO\\CO}>C(OH)_2$$

This reaction can also be applied to 1 : 3-diketohydrindene and to β-hydrindone (Chem. Soc. Trans. 1910, 97, 1438, 2025 ; 1911, 99, 792)

Triketohydrindene hydrate forms prisms from water which redden at 125°, give off gas at 139° and melt with decomposition at 239°–240°. The hydrate colours the skin red and reduces Fehling's solution. The diphenylhydrazone melts at 207°–208°, and the disemicarbazone darkens at 175° and melts with evolution of gas at 108°.

Triketohydrindene hydrate may be used as a reagent for proteins and their hydrolytic products (*cp.* Chem. Soc. Trans. 1911, 99, 798).

J. F. T.

INDIAN FIRE is a light used in pyrotechnical displays and for purposes of signalling. It is usually composed of 7 parts of sulphur, 2 of realgar, and 24 of nitre.

INDIAN GUM, or **GHATTI GUM**, is a gummy exudation from the stem of *Anogeissus latifolia* (Watt), occurring in vermiform or rounded tears, colourless pale yellow, and of a vitreous lustre; soluble in water forming a viscous adhesive mucilage; *v.* Gums.

INDIAN HEMP RESIN *v.* Resins.

INDIAN INK or **CHINESE INK.** This substance, used for writing or drawing, consists of lamp-black held together with animal or fish glue and dried in the form of cakes or sticks of paint. According to Chinese writers, the invention of ink is due to one Tien-Tchen who lived between 2697 and 2597 B.C. It is said by them that at that time the ink used was a kind of lacquer; later some kind of black stone rubbed in water came into use; lastly, about 250 years B.C., balls of lamp-black from the burning of lacquer and firewood, afterwards mixed with size, became the customary material. It is probable, however, that the Chinese became acquainted with the substance from the Coreans, to whom they are indebted for other useful arts. The material used for producing the lamp-black is in most instances fir timber, although many other media, such as rice treated with a decoction of *Hibiscus mutabilis* (Linn.), the bark of the pomegranate tree infused with vinegar, sesamé, rape seed, wood-oil, and rock-oil are employed, to which are added varnish and pork fat. The glue or size appears at the present day to be always obtained either from oxen or fish; the points of difference between various makers being (1) the mode of preparation; (2) the method of incorporation; and (3) the quantity relative to the amount of soot. Sometimes perfumed essences, as of musk or camphor, are added, especially in the choicest qualities. The paste is pressed into carved wooden moulds and, after baking, the sticks or other moulded forms are laid in a cool, dry place, and are said to improve with long keeping. The best ink is made from wood-oil lamp-black, and comes from the Anhui province.

The manufacture of Indian ink is also carried on in Japan, the following description, from a native source, indicating the method followed in that country: 'The body of the ink is soot obtained from pine-wood or resin, and lamp-black from sesamé oil for the finest sort. This is mixed with liquid glue made of ox-skin. This operation is effected in a large, round, copper bowl formed of two spherical calottes placed 1 inch apart, so that the space between can be filled up with hot water to prevent the glue from hardening during the time it is being mixed by hand with the lamp-black. The cakes are formed in wooden moulds, and dried between paper and ashes. Camphor, or a peculiar mixture of scents which come from China, and a small quantity of carthamine (the red colouring substance of safflower) are added to the best kinds for improving the colour as well as for scenting the ink.'

M. Merimée (De la Peinture à l'Huile) asserted that the Chinese do not use an animal but a vegetable size; but apparently without warrant. For a curious monograph compiled from native Chinese sources *v.* L'Encre de Chine, son Histoire et sa Fabrication d'après documents chinois traduits, par Maurice Jametel, Paris, 1882.

INDIAN PODOPHYLLUM RESIN *v.* Resins.

INDIAN RED. A mineral pigment from the Persian Gulf. In appearance it is a coarse powder of a purplish-red colour.

Howe's analysis of (1) the entire mineral, and of (2) that portion soluble in hydrochloric acid, gave

	SiO_2,	Fe_2O_3,	Al_2O_3,	CaO,	MgO,	SO_3,	CO_2,	H_2O	
(1)	30·17	56·59	3·79	2·65	1·43	2·28	1·73	1·62	= 100·26
(2)	—	3·19	2·22	2·65	0·87	2·28	1·73	—	= 12·94

(Edin. New Phil. Jour. New Series, 2, 306.)

The portion insoluble in hydrochloric acid is a ferric silicate $Fe_2O_3{\cdot}SiO_2$. A pseudo-Indian red is composed principally of sesquioxide of iron.

INDIAN VALERIAN RHIZOME. The dried rhizome of *Valeriana Wallichii*.

INDIAN YELLOW, PIURI, PURREE, or **PIOURY,** is a pigment mainly used in India for colouring walls, doors, and lattice-work, and by artists for water-colour work. On account of its disagreeable smell it is but rarely employed as a dyestuff. It is, or was, made almost exclusively at Monghyr in Bengal, and is obtained from the urine of cows which have been fed upon mango leaves. On heating the urine, usually in an earthen pot, the colouring matter separates out; this is pressed into a ball and dried partly over a charcoal fire and finally in the sun. It sold on the spot at about 1 rupee per lb. and is, or was, mainly sent to Calcutta and Patna. One cow produces, on the average, 3·4 litres of urine per diem, yielding 2 ozs. (56 grams) of piuri. The yearly production is stated to have been from 100 to 150 cwts., which was probably over-estimated (*v.* Journ. Soc. Arts, 1883, [v.] 32, 16, and Annalen, 254, 268).

Piuri occurs in commerce in the form of round balls, which internally are of brilliant yellow colour, whereas the outer layers are either brown or of a dirty-green colour. The substance has a characteristic urinous smell. The undecomposed part consists only of *euxanthic acid* ($C_{19}H_{18}O_{11}$) in the form of a magnesium or calcium salt; the outer and decomposed portion contains in addition *euxanthone*, both free and combined. The composition of piuri seems to be variable; a fine sample, according to Graebe, contained

Euxanthic acid . .	51·0
Silicic acid and alumina . .	1·5
Magnesium . . .	4·2
Calcium . . .	3·4
Water and volatile matter .	39·0
	99·1

Euxanthic acid is easily obtained by digesting piuri of good quality with dilute hydrochloric acid and treating the residue with a solution of ammonium carbonate. On the addition of hydrochloric acid to the filtered solution euxanthic acid crystallises out with $1H_2O$ in glistening straw-yellow needles, melting at 162°. Euxanthic acid is, according to Spiegel, decomposed by hydrochloric acid into glycuronic acid and euxanthone: $C_{19}H_{18}O_{11}=C_{13}H_8O_4+C_6H_{10}O_7$. Külz, in order to prove the animal origin of euxanthic acid, gave euxanthone to rabbits and dogs, and was able to detect euxanthic acid in the urine. Külz's experiments did not corroborate Schmid's statement that mangostin (obtained from *Garcinia mangostana*, Linn.) is similarly converted into euxanthic acid by animals (E. Külz, Zeitsch. Biol. 33, 475; J. Soc. Chem. Ind. 6, 507).

Although the potassium and sodium salts of euxanthic acid are of the type $C_{19}H_{17}O_{11}M$, the silver salt obtained from the potassium salt by silver nitrate has the composition $C_{19}H_{15}O_{10}Ag$, and is derived from an anhydride of the acid (*Anhydroeuxanthic acid*); the methyl and ethyl esters prepared from the silver salt are of the same type (Graebe, Ber. 1900, 53, 3360).

Potassium euxanthate $C_{19}H_{17}O_{11}K,H_2O$ crystallises readily from water, and is prepared by neutralising euxanthic acid with potassium carbonate.

Magnesium euxanthate $C_{19}H_{16}O_{11}Mg,5H_2O$ is the main constituent of Indian yellow (Graebe, Annalen, 254, 268).

Barium euxanthate $Ba(C_{19}H_{17}O_{11})_2,9H_2O$ is soluble in boiling water, and on cooling separates in the gelatinous condition.

Silver anhydroeuxanthate $C_{19}H_{15}O_{10}Ag$ behaves similarly.

Ethylanhydroeuxanthate $C_{19}H_{15}O_{10}C_2H_5$, yellow-coloured needles, melts at 198°.

Tetra-acetylethylanhydroeuxanthate

$$C_{19}H_{11}O_{10}C_2H_5(C_2H_3O)_4$$

colourless needles, melts at 216°.

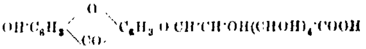
Methyl anhydroeuxanthate $C_{19}H_{15}O_{10}CH_3$, melts at 218°, and closely resembles the ethyl derivative.

Benzoyl-anhydroeuxanthate

$$C_{19}H_{11}O_{10}(CO-C_6H_5)_5$$

melts at 194°, but has not yet been crystallised.

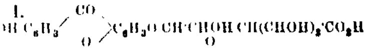
The constitution of euxanthic acid is expressed by Graebe (Annalen, 254, 267) as



$$OH\cdot C_6H_3\left\langle\begin{matrix}O\\CO\end{matrix}\right\rangle C_6H_3\cdot O\cdot CH\cdot CH\cdot OH(CHOH)_4\cdot COOH$$

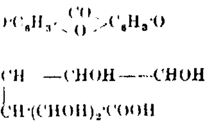
whereas for that of anhydroeuxanthic acid one of the following two formulæ is suggested:—

I.



$$OH\cdot C_6H_3\left\langle\begin{matrix}CO\\O\end{matrix}\right\rangle C_6H_3\cdot O\cdot CH\cdot \underset{O}{CHOH}\cdot CH(CHOH)_2\cdot CO_2H$$

II.



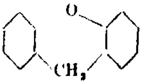
$$\begin{array}{l}O\cdot C_6H_3\left\langle\begin{matrix}CO\\O\end{matrix}\right\rangle C_6H_3\cdot O\\ \\ CH\;-CHOH-\!\!-CHOH\\ \big|\\ CH\cdot(CHOH)_2\cdot COOH\end{array}$$

Euxanthone, Purrenone, Purrone $C_{13}H_8O_4$ was first obtained by Stenhouse (Annalen, 51, 425), and soon afterwards by Erdmann (*ibid.* 52, 365), from euxanthic acid. It crystallises in pale yellow needles or laminæ, melting at 240° (corr.), which sublime with little decomposition on gentle heating.

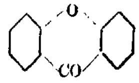
Diacetyl-euxanthone, pale yellow prisms (Salzmann and Wichelhaus, Ber. 1877, 10 1397), melts at 185°.

By distillation with zinc-dust (Salzmann and Wichelhaus; Graebe and Ebrard, Ber. 16, 75) euxanthone gives *methylenediphenylene oxide* (I.), which by oxidation is converted into xanthone (II.), indicating that euxanthone possesses the

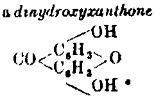
I.



II.

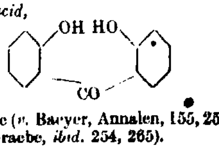


constitution of a *dihydroxyxanthone* (S. and W.).



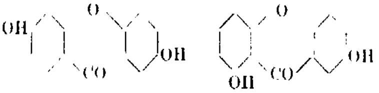
$$CO\left\langle\begin{matrix}C_6H_3\\C_6H_3\end{matrix}\right\rangle O \quad \text{(each } C_6H_3\text{ with } OH)$$

When fused with alkali euxanthone yields *euxanthonic acid*,



hydroquinone (*v.* Baeyer, Annalen, 155, 257), and resorcinol (Graebe, *ibid.* 254, 265).

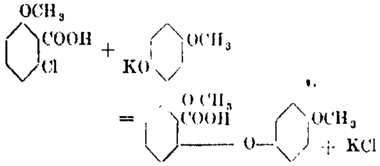
The first synthesis of euxanthone is due to Graebe (*l.c.*) who accomplished this by distilling a mixture of β-resorcylic acid and hydroquinone carboxylic acid, and it was shown later by *v.* Kostanecki and Nessler (Ber. 1891, 24, 3983), that if in this reaction the β-resorcylic acid is replaced by resorcinol the same product is obtained. As the result of these syntheses two constitutional formulæ for euxanthone were possible:



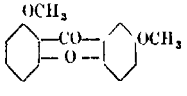
I II

When methylated by means of methyl iodide in the usual manner (*v.* Kostanecki, Ber. 1894, 27, 1992), euxanthone yields only a *monomethyl ether* $C_{13}H_7O_3(OCH_3)$ (yellow plates, m.p. 129°), and this on treatment with strong sodium hydroxide solution gives an insoluble yellow sodium salt. The latter, by washing with water, is decomposed with regeneration of the free monomethyl ether. These reactions indicate that euxanthone contains an hydroxyl in the ortho-position to a carboxyl group (*cf.* also Herzig, Monatsh. 12, 161), and that, therefore, its constitution is represented by formula II. The final proof of this formula is afforded by a later synthesis of euxanthone (Ullmann and Panchaud, Annalen, 350, 108).

2-Chloro-6-methoxybenzoic acid is condensed with the potassium derivative of hydroquinone monomethyl ether, employing copper powder as a catalyst

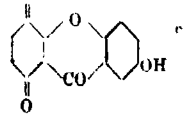


The resulting 4-*methoxy-2-phenoxy-6-methoxy benzoic acid* when treated with concentrated sulphuric acid is converted into *euxanthone dimethyl ether*

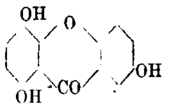


and this by treatment with aluminium chloride in the presence of benzene gives euxanthone

According to Neirenstein (Ber 1913, 46, 640) by oxidising euxanthone with chromic acid the quinone



is produced. This consists of dark-red needles soluble in alkali with a blue coloration, and on reduction is converted into 2 : 5 : 8 trihydroxyxanthone, pale yellow needles, m.p. 328°–330°.



The triacetyl derivative melts at 226°–230°.

Disazobenzene-euxanthone $C_{13}H_6O_4(C_6H_5N_2)_2$ (Perkin, Chem. Soc. Trans. 73, 666), red needles, m.p. 249°–250° (decomp.), is readily prepared by adding diazobenzene sulphate to a weak alkaline solution of euxanthone.

Acetyldisazobenzene-euxanthone, ochre-yellow needles, melts at 197°–199°.

Euxanthone possesses only feeble tinctorial properties; the respective shades obtained with woollen cloth mordanted with chromium, aluminium, and tin being dull brown-yellow, pale bright yellow, and very pale bright yellow (Perkin and Hummel, Chem. Soc. Trans. 1896, 69, 1290). A. G. P.

INDIARUBBER or **CAOUTCHOUC** *v.* RUBBER.

INDICAN *v.* GLUCOSIDES; INDIGO, NATURAL.

INDICANURIA *v.* INDOXYL COMPOUNDS.

INDICATORS *v.* ACIDIMETRY AND ALKALIMETRY; also art. ANALYSIS.

INDIGO, NATURAL. Indigo has been known in Asia from a remote period of antiquity, and there exist very ancient records in Sanskrit describing its methods of preparation. The Romans appear to have recognised it only as a pigment (*indicum*), but evidence as to its use as a dye by the ancient Egyptians has been abundantly proved from the examination of mummy cloths. Its employment in Europe was very limited until in 1516 when it began to be imported from India by way of the Cape of Good Hope, but its introduction in large quantity did not occur until about 1602. Owing chiefly to the opposition of the growers of woad, its European rival, as a dyeware it met with much opposition, and various laws were enacted both on the Continent and in England prohibiting its use. It was called a 'devilish drug,' and was said to be injurious to fabrics. In 1737 its employment was legally permitted in France, and from this period its valuable properties appear to have become gradually recognised throughout Europe.

The most important plants which yield indigo are those of the genus *Indigofera* belonging to the natural order of the *Leguminosæ*; these have been cultivated in India, China, Egypt, the Philippines, Caracas, and Brazil.

For the purpose of indigo manufacture the *Indigofera tinctoria* (Linn.), *I. sumatrana* (Garrtn.) (the Indian plant), *I. dispernma* (Linn.), *I. argentea* (Linn.), and *I. arrecta* (Hochst.) (the Natal plant), the *I. paucifolia* (Delile) (Madagascar plant), and *I. secundiflora* (Poir.) (Guatemala plant), have been mainly used, though certain less valuable varieties, viz. the *I. pseudotinctoria* (R. Br.), *I. angustifolia* (Linn.), *I. arcuata* (Willd.), *I. caroliniana* (Walt.), *I. cinerea* (Willd.), *I. longeracemosa* (Boiv.), *I. cærulea* (Roxb.), *I. endecaphylla* (Jacq.), *I. glabra* (Linn.), *I. hirsuta* (Linn.), *I. indica* (Lam.), *I. mexicana* (Benth.), *I. leptostachya* (DC.), have been employed. In Japan, China, and Russia the plant usually cultivated has been the *Polygonum tinctorium* (Ait.), but the *Isatis tinctoria* (Linn.), or woad plant, at one time very largely grown in Europe, is now only used in very limited quantity as an adjunct in the dyeing of indigo (woad vat). The native source of indigo in Western Africa appears to consist almost entirely of the *Lonchocarpus cyanescens* (Benth.) (Perkin, J. Soc. Chem. Ind. 1907, 26).

Other indigo-yielding plants are the *Nerium tinctorium*, *Gymnema tingens* (Spreng.), *Eupatorium laeve* (DC.), *Tephrosia tinctoria* (Pers.), *Marsdenia tinctoria* (R. Br.), and certain species of orchids such as the *Phaius grandiflorus* (Reich.), and *Calanthe veratrifolia* (R. Br.).

In addition to these, various plants of which the *Mercurialis perennis* (Linn.), *Fagopyrum esculentum* (Moench.), *Fraxinus excelsior* (Linn.), *Baptisia tinctoria* (R. Br.), and *Rhamnus alaternus* (Linn.) (Georgievics, Der Indigo, 1892) may be given as examples, are stated to yield indigo, or a very similar colouring matter, but this requires confirmation.

The production of indigo from the indigo plant is of a simple character and consists mainly of two processes, viz. a steeping of the plant with water (fermentation), followed by the oxidation of the solution with air in a separate vessel. Until very recently but little modification appears to have been introduced into this ancient process, and there is also but little variation to be found in the main features as described by Bancroft (Philosophy of Permanent Colours, 1813), Crookes (Manual of Dyeing and Calico Printing, 1874), Bridges-Lee (Indigo Manufacture, 1892), Georgievics (*l.c.* 1892), and Rawson (The Cultivation and Manufacture of Indigo, J. Soc. Dyers, 1899).

Directly the plants are cut down they are tied in bundles and brought to the factory without delay, because it is necessary that the material should be operated on at once.[1] The tanks for the extraction (steeping vats) and precipitation of the indigo by oxidation (beating vats) are sometimes of stone, but more usually of brickwork lined inside with cement, and are respectively ranged in two rows one above the other, so that the former can be drained into the latter. The steeping vats may have a capacity of about 1000 cub. ft., and are usually of much smaller dimensions than the beating vats, of which less are consequently required. According to Rawson (*l.c.*), who describes a small indigo factory, each range of beating vats runs the whole length of six steeping vats, and has a width of 13 feet 6 inches.

Into each of the upper tanks the bundles of the plant are tightly packed (preferably in a horizontal position, Bridges-Lee, *l.c.*), on the top of this is laid a horizontal trellis of bamboo, and the whole is wedged down into the tanks by means of timber, so that the material is unable to float during the fermentation process. Water is then run in, in such quantity that the bundles are entirely submerged. After about two hours an active fermentation is observed, and the surface of the liquid becomes covered with froth owing to the evolution of a mixture of carbon dioxide, oxygen, and nitrogen (Georgievics, *l.c.*); in the later stages (Rawson, *l.c.*) either marsh gas or hydrogen or a mixture of the two is freely produced. After 10–15 hours, according to the prevailing temperature of the water, the straw-yellow, orange, or olive-green coloured liquid is drawn off into the tanks below, and submitted to oxidation with air.

This may be accomplished by 'hand beating,' by machinery (the beating wheel), by blowing air through the liquid, or by the shower-bath method. During this operation the colour of the liquid gradually changes, becoming first dark green and then blue, and considerable frothing is produced. When it is observed that the indigo precipitate or 'fecula' readily settles, the beating is discontinued and the mixture allowed to rest for some two hours. The supernatant liquid, or 'seeth water,' having been drained off as completely as possible, the indigo sludge or 'mal' is led into a reservoir inside the factory, from which it is subsequently elevated by means of a hand pump or steam injector into a large cauldron known as the 'mal boiler.' It is here heated by direct fire or by the admission of steam, and this has for its object the prevention of a further fermentation, the solution of certain brown impurities, and a more complete granulation of the 'mal.'

The product is then run on to a filter known as a 'table,' consisting of stout cotton or linen cloth stretched over a shallow rectangular basin of stone or cement, with a drainage opening at one corner, and allowed to remain until it has the consistency of a stiff paste. In order to remove excess of moisture the indigo is transferred to perforated wooden boxes lined with sail cloth and cautiously pressed. Finally, the resulting slab is cut into cakes by means of a guillotine or metal wires and allowed to dry at the ordinary temperature on trellis-work shelves in a specially constructed drying house.

THE PLANT.

Until the last few years the *I. sumatrana* appears to have been exclusively employed in the best-conducted factories in India. According to Leake (Report of the Dalsingh Serai Research Station, 1903–1904) this is a mixture of several sub-varieties of different values. In this, as in apparently all other indigo plants, the indican exists exclusively in the leaf, though Bloxam and Leake (*l.c.*) point out that the midrib or rachis also contains the glucoside. For the manufacture of indigo the main points in connection with the plant are the weight yielded per acre, the percentage of leaf present, and the

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[1] It has long been known that the percentage of indican rapidly disappears from the leaf in the freshly plucked moist condition, and on this account it is advisable that the plant when cut down should be dealt with at once. On the other hand, it has been the practice to a small extent in certain districts to air-dry the leaf before proceeding with the manufacture of indigo. In order to determine if when air-dried under ideal conditions, the leaf in these circumstances loses a material amount of indican, experiments were made by Watson (Jour. Chem. Soc. Ind. 1918, 37, 81) with indigo plant specially grown for the purpose. The leaf when gathered was divided into two portions, one of which was analysed at once, and the second dried by spreading in a thin layer upon filter paper in a north verandah for three or four days until constant in weight.

The analyses were carried out by the isatin method (*l.c.*) with 10 grammes of leaf weighed in each case in the fresh condition, and the results expressed as indirubin indicate that a serious loss of colouring principle does occur in these circumstances:—

	Fresh Leaf.	*Air-dried Leaf.*
(*a*)	0·1008	0·0568
(*b*)	0·0625	0·0610
(*c*)	0·1057	0·0703

indigotin-producing value of the latter. According to Rawson (Cultivation and Manufacture of Indigo, *l.c.*) the good plant contains 40 p.c. of leaf, though occasionally, but not often, the proportion of leaf rises to as much as 60 p.c. Bloxam and Leake found, however, much higher values, 51·7–61·6 on ordinary Indian plant, and 65 p.c. given by twelve experimental plots, figures which include the rachis. Bergtheil (Report of the Indigo Research Station, Sirsiah, 1906, 8) found the percentage of leaf to be 40 p.c., and never higher than 45 p.c.; but, on the other hand, in a redetermination, Leake (J. Soc. Chem. Ind. 1907, 26, 1174) records the value as 62·2 p.c. Rawson, who conducted numerous analyses of the leaf by his persulphate process (*l.c.*), shows that the indican content as expressed by indigo-yielding capacity varies at different periods of the year. Thus, whereas in one instance on May 28 the figure was 0·20 p.c., on August 25 this had risen to 0·76 p.c. of indigotin. Though the leaf on a young plant gives but a small percentage of colouring matter, yet as the plant grows the new leaf contains more colouring principle than the old on the same plant. As an example, on one occasion the percentages of indigotin recorded with new and old leaf were respectively 0·71 and 0·35 p.c. Finally, there is a gradual increase in colouring matter given by leaves from the bottom of the plant upwards as represented by the figures 0·30, 0·44, and 0·62 p.c. respectively. According to Bergtheil (Report of the Indigo Research Station, 1907, 3) the 'indigotin content' of the plant is rarely so high as 0·3 p.c. Though the leaf, as a rule, contains a maximum of colouring matter from about the middle to the end of August, it does not necessarily follow that this is the best period for manufacture, as by this time the plant will usually have lost a considerable portion of leaf (Rawson). The manufacture, indeed, usually commences about the middle of June. Gaunt, Thomas, and Bloxam (J. Soc. Chem. Ind. 1907, 26, 1174) refer to a sample of the air-dried leaves of the *I. sumatrana*, which, in comparison with other dry samples of the same variety (0·6 approx.) and of the Java plant, *I. arrecta* (1·81 p.c.), yielded indigotin to the value of 3·53 p.c., and consider that this indicates that by selection and suitable methods of cultivation it should be possible to obtain an average plant of greater indigo-producing power than has hitherto been the case.

The plant formerly employed by the Java planters was the *I. secundiflora*, 'Guatemala plant,' but for several years past this has been replaced by the *I. arrecta* or 'Natal plant.' The latter, it is stated, contains not only more leaf than the ordinary Indian plant, but, as a rule, the leaf yields also a considerably larger percentage of indigo. More recently the Indian planters have recognised the value of the *I. arrecta*, and accounts are given by Coventry (Indigo Improvements Syndicate Report, 1901) of experiments in connection with its introduction. Leake (Dalsingh Serai Report, 1905) discusses the difficulties of the germination of the seed of the Natal-Java plant, which is due to the impermeable character of the seed-coat. This defect, it is pointed out, can be overcome by a process of scratching, and a practical method for this purpose is described. Bergtheil (*l.c.*), in conjunction with D. L. Day, treats the seed with strong sulphuric acid, which leads either to a swelling of the seed coat and its eventual rupture or converts it into a body akin to cellulose and permeable to water. Analyses of the indigo-yielding power of this leaf by Rawson (*l.c.*) gave figures up to 0·96 p.c., whereas Bergtheil (*l.c.* 1906) finds in comparison to the *I. sumatrana* (0·585) that the *I. arrecta* produced 1·05 p.c. of colouring matter. The percentage of leaf given by the latter averages 52·2 p.c. Again, in 1909 the yield from 100 maunds of the *I. arrecta* was 15 seers 10 chittacks, as against 11 seers 14 chittacks from the same quantity of the *I. Sumatrana*. The Natal plant is now established in India, and its value appears to be fully recognised. According to Bergtheil (1907) the indigo made from the Java plant has generally been of a high indigotin content, and (1906) that whereas the yield of indigo per acre was 12·6 'seers,' that given by the *I. sumatrana* was by comparison only 8 seers.

An account of recent work on the indigo plant by W. A. Davis is given in the Indigo Publications (1918–21) of The Agricultural Research Institute, Pusa. Davis attributes (Publ. Nos. 1 & 2) the progressive deterioration of the indigo crops during the last twenty years chiefly to the fact that the soils are exhausted as regards phosphate. The good effects of phosphate manuring is confirmed by experiment (*cf.* also Publ. No. 6), and there can thus be no doubt that the continuous and systematic treatment of the soil with superphosphate is essential for the proper cultivation of the indigo plant. Dealing particularly with the Java indigo plant (Publ. No. 7), it is stated (see p. 32) that:—

"High quality plant rich in indigotin is obtained when the soil is poor in nitrogen, so that the plant is forced to grow on nitrogen taken up from the air by the nodule bacteria. It seems probable that the activity of these organisms determines high indigotin content, and that the production of indican is due to the plant removing from the nodules nitrogen compounds which would be prejudicial to their continuous action.'

The factors which make for development of the nodules are: (1) low nitrogen in soil; (2) good supply of soluble phosphate; (3) good supply of organic matter (yielding carbohydrates).

Care must be taken in supplying humus not to supply nitrogen. Thus a manure such as seet, whilst giving high yields of plant per acre, gives leaf poor in indican content. The use of cover crops (*e.g.* wheat or mustard) grown with indigo, which remove nitrogen from the soil, is advantageous.

THE CHEMISTRY OF NATURAL INDIGO MANUFACTURE.

According to the early researches of Chevreul (Ann. Chim. Phys. 1808, 66, 8, and 1808, 68, 284) and of Geradin and Preisser (J. Pharm. Chim. 1840, 26, 344) the colouring principle of indigotin present in indigo-yielding plants was considered to consist of indigo white, and this theory remained uncontradicted until Schunck (Phil. Mag. 1855, [iv.] 17, 74, and 1858, 15, 127) isolated from the *Isatis tinctoria* (woad), *Polygonum tinctorium*, and *Indigofera tinctoria* the *Polygonum tinctorium* (Ait.), but the *Isatis tinctoria* (Linn.), or woad plant, at one time very largely grown in Europe, is now only used in very limited quantity as an adjunct in the dyeing of indigo (woad vat). The native source of indigo in Western Africa appears to consist almost entirely of the *Lonchocarpus cyanescens* (Benth.) (Perkin, J. Soc. Chem. Ind. 1907, 26).

Other indigo-yielding plants are the *Nerium tinctorium*, *Gymnema tingens* (Spreng.), *Eupatorium laeve* (DC.), *Tephrosia tinctoria* (Pers.), *Marsdenia tinctoria* (R. Br.), and certain species of orchids such as the *Phaius grandiflorus* (Reich.), and *Calanthe veratrifolia* (R. Br.).

In addition to these, various plants of which the *Mercurialis perennis* (Linn.), *Fagopyrum esculentum* (Moench.), *Fraxinus excelsior* (Linn.), *Baptisia tinctoria* (R. Br.), and *Rhamnus alaternus* (Linn.) (Georgievics, Der Indigo, 1892) may be given as examples, are stated to yield indigo, or a very similar colouring matter, but this requires confirmation.

The production of indigo from the indigo plant is of a simple character and consists mainly of two processes, viz. a steeping of the plant with water (fermentation), followed by the oxidation of the solution with air in a separate vessel. Until very recently but little modification appears to have been introduced into this ancient process, and there is also but little variation to be found in the main features as described by Bancroft (Philosophy of Permanent Colours, 1813), Crookes (Manual of Dyeing and Calico Printing, 1874), Bridges-Lee (Indigo Manufacture, 1892), Georgievics (*l.c.* 1892), and Rawson (The Cultivation and Manufacture of Indigo, J. Soc. Dyers, 1899).

Directly the plants are cut down they are tied in bundles and brought to the factory without delay, because it is necessary that the material should be operated on at once.[1] The tanks for the extraction (steeping vats) and precipitation of the indigo by oxidation (beating vats) are sometimes of stone, but more usually of brickwork lined inside with cement, and are respectively ranged in two rows one above the other, so that the former can be drained into the latter. The steeping vats may have a capacity of about 1000 cub. ft., and are usually of much smaller dimensions than the beating vats, of which less are consequently required. According to Rawson (*l.c.*), who describes a small indigo factory, each range of beating vats runs the whole length of six steeping vats, and has a width of 13 feet 6 inches.

Into each of the upper tanks the bundles of the plant are tightly packed (preferably in a horizontal position, Bridges-Lee, *l.c.*), on the top of this is laid a horizontal trellis of bamboo, and the whole is wedged down into the tanks by means of timber, so that the material is unable to float during the fermentation process. Water is then run in, in such quantity that the bundles are entirely submerged. After about two hours an active fermentation is observed, and the surface of the liquid becomes covered with froth owing to the evolution of a mixture of carbon dioxide, oxygen, and nitrogen (Georgievics, *l.c.*); in the later stages (Rawson, *l.c.*) either marsh gas or hydrogen or a mixture of the two is freely produced. After 10–15 hours, according to the prevailing temperature of the water, the straw-yellow, orange, or olive-green coloured liquid is drawn off into the tanks below, and submitted to oxidation with air.

This may be accomplished by 'hand beating,' by machinery (the beating wheel), by blowing air through the liquid, or by the shower-bath method. During this operation the colour of the liquid gradually changes, becoming first dark green and then blue, and considerable frothing is produced. When it is observed that the indigo precipitate or 'fecula' readily settles, the beating is discontinued and the mixture allowed to rest for some two hours. The supernatant liquid, or 'seeth water,' having been drained off as completely as possible, the indigo sludge or 'mal' is led into a reservoir inside the factory, from which it is subsequently elevated by means of a hand pump or steam injector into a large cauldron known as the 'mal boiler.' It is here heated by direct fire or by the admission of steam, and this has for its object the prevention of a further fermentation, the solution of certain brown impurities, and a more complete granulation of the 'mal.'

The product is then run on to a filter known as a 'table,' consisting of stout cotton or linen cloth stretched over a shallow rectangular basin of stone or cement, with a drainage opening at one corner, and allowed to remain until it has the consistency of a stiff paste. In order to remove excess of moisture the indigo is transferred to perforated wooden boxes lined with sail cloth and cautiously pressed. Finally, the resulting slab is cut into cakes by means of a guillotine or metal wires and allowed to dry at the ordinary temperature on trellis-work shelves in a specially constructed drying house.

THE PLANT.

Until the last few years the *I. sumatrana* appears to have been exclusively employed in the best-conducted factories in India. According to Leake (Report of the Dalsingh Serai Research Station, 1903–1904) this is a mixture of several sub-varieties of different values. In this, as in apparently all other indigo plants, the indican exists exclusively in the leaf, though Bloxam and Leake (*l.c.*) point out that the midrib or rachis also contains the glucoside. For the manufacture of indigo the main points in connection with the plant are the weight yielded per acre, the percentage of leaf present, and the

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[1] It has long been known that the percentage of indican rapidly disappears from the leaf in the freshly plucked moist condition, and on this account it is advisable that the plant when cut down should be dealt with at once. On the other hand, it has been the practice to a small extent in certain districts to air-dry the leaf before proceeding with the manufacture of indigo. In order to determine if, when air-dried under ideal conditions, the leaf in these circumstances loses a material amount of indican, experiments were made by Watson (Jour. Chem. Soc. Ind. 1918, 37, 81) with indigo plant specially grown for the purpose. The leaf when gathered was divided into two portions, one of which was analysed at once, and the second dried by spreading in a thin layer upon filter paper in a north verandah for three or four days until constant in weight.

The analyses were carried out by the isatin method (*l.c.*) with 10 grammes of leaf weighed in each case in the fresh condition, and the results expressed as indirubin indicate that a serious loss of colouring principle does occur in these circumstances:—

	Fresh Leaf.	*Air-dried Leaf.*
(*a*)	0·1008	0·0568
(*b*)	0·0625	0·0610
(*c*)	0·1057	0·0703

In a paper by Beyerinck (Proc. K. Akad. Wetensch. Amsterdam, 1900, 3, 102), 'On the Formation of Indigo from Woad,' this chemist discusses Schunck's well-known work on the same subject, and points out that the indigo-yielding substance contained in this plant is not, as Schunck regarded it, identical with the indican present in the *Polygonum tinctorium.* The colouring principle of woad Beyerinck names *isatan*, and shows that this compound, unlike indican, is decomposed in feebly alkaline solutions, whereas indican is stable even in concentrated alkaline liquids. In presence of acids both isatan and indican are hydrolysed, but indican with greater difficulty. *Isatase*, the specific enzyme of woad, does not act on indican, and isatan, on the other hand, is unaffected both by the indigo enzyme or by common bacteria.

Schunck (Chem. News, 1900, 82, 176) considered that the crystalline indican of Hoogewerff and ter Meulen was not the substance obtained by him, and should not be considered as a pure variety of it, but was rather derived from it, by extracting the plant with a hot solvent and the use of chemicals. He preferred to name his compound *a*-indican and theirs *b*-indican.

Bergtheil (Chem. Soc. Trans. 1904, 85, 877), who experimented with the *I. sumatrana* and *I. arrecta*, did not find it possible to prepare indican from the leaves of these plants in the manner described by Hoogewerff and ter Meulen.

It was, however, shown by Perkin and Bloxam (Chem. Soc. Trans. 1907, 91, 1715) that crystalline indican can be isolated from both of these plants by such a method, and is in reality the source of the natural indigo which is derived from them.

In a further communication ter Meulen (Rec. trav. chim. 1905, 29, 444) describes a modification of the method previously given for the isolation of indican from the *Polygonum tinctorium*, which consists in treating a cold solution of the partially purified substance with sulphuric acid, by which means certain impurities are precipitated. The acid is then removed with barium carbonate. The main object of the investigation was, however, the determination of the sugar that this glucoside yields when hydrolysed by its specific enzyme, and this proved to be dextrose, as already indicated by Hazewinkel (*l.c.*).

As a result of the study of the behaviour of indican with solvents, Perkin and Bloxam (*l.c.*) devised a very simple process for the isolation of this glucoside, by the aid of which large quantities of the pure substance could be readily prepared.

The leaves and stems of the *I. sumatrana* (1000 grams) were treated with 4 litres of cold acetone, the mixture being occasionally shaken during 7 days, and the green-coloured extract was evaporated on the steam bath to a very small bulk. To the residue light petroleum was added, causing the deposition of a brown viscous precipitate of crude indican, and this was repeatedly agitated with small quantities of light petroleum. The product on treatment with water gave a pale yellow liquid, containing resinous matter in suspension, and the latter was removed by shaking with ether. The clear aqueous solution, treated with 10 c.c. *N*/2 sodium carbonate, on gradual evaporation *in vacuô* deposited crystals, and eventually a semi-solid mass was obtained. It was collected, drained, and allowed to dry at the ordinary temperature. When exhaustively extracted, 1000 grams of leaf gave 31·66 grams of indican, and by a continuous system of working more than 500 grams of crystalline indican were prepared. The preparation of this glucoside from the leaves of *I. arrecta* is more troublesome, owing partly to the presence of kaempferitrin (*l.c.*), but more especially of a colourless sugar-like compound $C_6H_{12}O_5$; m.p. 186°–187°; possibly a modification of quercitol. The fact that indican can be so readily isolated without the aid of heat, and merely with the use of acetone, light petroleum and ether, is not in harmony with the contention of Schunck (*l.c.*) that the crystalline glucoside is an alteration product of his amorphous substance, and consequently the terms α- and β-indican suggested by him should disappear.

Indican crystallised from water

$$C_{14}H_{17}O_6N,3H_2O$$

melts at 57°–58°, but in the anhydrous condition as obtained by the addition of boiling benzene to its hot alcoholic solution, at 176°–178°. Owing to its somewhat ready solubility in water it can be more economically purified by the latter process, and, according to Perkin and Thomas (Chem. Soc. Trans. 1909, 95, 793), crystallisation from absolute alcohol gives excellent results.

A newer method of preparing indican from indigo-yielding plants, in which acetone is also employed, has been devised by B. M. Amin (Agr. Res. Inst., Pusa, Indigo Publ. No. 5). The fresh leaf is extracted with hot water, and freshly slaked lime added to precipitate impurities. These are removed, the filtrate evaporated and extracted with acetone. By evaporation and cooling in ice indican hydrate separates from the aqueous solution. Dissolved in absolute alcohol, and by precipitation with benzene (*cf.* Perkin and Bloxam) pure anhydrous indican crystallises (yield 70–80 p.c.). This method is specially suitable for preparing pure indican in large quantities from the Java indigo plant (*I. arrecta*) for which Perkin and Bloxam's method is hardly serviceable. The advantages claimed by this method are its rapidity, its general application and the small amount of organic solvent required.

It has been shown by Baeyer (Ber. 1881, 14, 1745) that indoxyl readily condenses with aldehydes and ketones to form the so-called *indogenides*, and Hazewinkel (*l.c.*) partly identified this substance by means of its condensation products with isatin, benzaldehyde, and pyruvic acid, relying, however, on their qualitative reactions, as he did not prepare these compounds in a pure enough condition for analysis. Almost simultaneously Beyerinck (Proc. K. Akad. Wetensch. Amsterdam, 1899, 2, 120) prepared indirubin by hydrolysing crude indican in the presence of isatin.

Perkin and Bloxam (*l.c.*) and Gaunt, Thomas, and Bloxam (J. Soc. Chem. Ind. 1907, 26, 1174), who experimented with the pure substance, found that when indican dissolved in water is added to a boiling solution of isatin, acidified with a little hydrochloric acid, and the operation is carried out in an atmosphere of hydrogen or carbon dioxide, the yield of indirubin is quantitative according to the following equations :—

$$C_{14}H_{17}O_6N+H_2O=C_8H_7NO+C_6H_{12}O_6$$
$$C_8H_7NO+C_8H_5NO_2=C_{16}H_{10}N_2O_2+H_2O$$

This 'isatin' method, for details of which see later, affords a ready means, not only for the analysis of the crystalline glucoside, but also for the estimation of the amount which is present in aqueous infusions of the leaf (*v. infra*).

More recently Perkin and Thomas (Chem. Soc. Trans. 1909, 95, 795), who studied in a similar way the condensation of indoxyl derived from indican with *p*-nitrobenzaldehyde, found that the *p*-nitrobenzaldehydeindogenide is deposited in quantitative amount, and that this reaction could also be employed for the analysis, both of crystalline indican and of that present in the leaf extract. The reaction takes place with extreme readiness, for with indican solution at a dilution of 1 in 1000, the above compound quickly separates, and even at 1 in 10,000 the condensation can be observed to take place. Piperonal and indican in the presence of dilute acid yield the analogous compound $C_{16}H_{11}O_3N$, orange-coloured needles, m.p. 223°-224°, but this process, under analytical conditions, gave only approximately satisfactory results. As a side issue, *p*-hydroxybenzaldehydeindogenide $C_{15}H_{11}O_2N$ orange-red needles, m.p. 267°-269°, and dihydroxybenzaldehydeindogenide

$$C_{15}H_{11}O_3N$$

orange-red needles, m.p. 264°-265°, were prepared from indican. The latter compound derived from protocatechuic aldehyde dissolves in concentrated sodium hydroxide, with a bluish violet coloration, and dyes with mordanted woollen cloth well-defined shades.

On the other hand, when indican is hydrolysed with acid in the presence of an oxidising agent it does not appear possible to obtain a quantitative yield of indigotin. Hazewinkel (*l.c.*) states, in regard to this point, that acid oxidising agents convert indican into indigo, and this in turn is oxidised by an excess of the reagent. By the use of ferric chloride and hydrochloric acid, Hoogewerff and ter Meulen obtained from the pure glucoside only 91 p.c. of the theoretical quantity of colouring matter, which appeared to contain indirubin, and was of doubtful purity. Gaunt, Thomas, and Bloxam (*l.c.*), who examined the behaviour of ammonium persulphate, a reagent suggested by Rawson for the analysis of the plant extract (Report on the Cultivation and Manufacture of Indigo, Mozzufferpore, 1904; *cf.* also Bloxam and Leake, Dalsingh Serai Report, 1904), found that the process was far from quantitative with pure indican, and that the yield of colouring matter averaged but 82 p.c. of the theoretical. Perkin and Thomas (*l.c.*) studied the effect of the hydrolysis of solutions of indican with acid during the aspiration of air through the liquid, under varying conditions of temperature and concentration. The most satisfactory yield of pure colouring matter (93·5 p.c.) was produced when air was passed during eight hours through a solution of 0·5 gram of the glucoside in 850 c.c. of water acidified with 15 c.c. of 33 p.c. hydrochloric acid, and the temperature maintained at 60°.

When, however, the operation was carried out at 70° less colouring matter was obtained (87·6 p.c.), and, curiously enough, replacement of the hydrochloric acid by an equivalent amount of sulphuric acid gave, under similar conditions, a much lower result. The deficiency in the yields given by these air oxidation processes was due to the fact that a portion of the indoxyl had been converted into substances other than indigotin, and it was observed that whereas in the case of hydrochloric acid the filtrate possessed a pale yellow colour, that containing sulphuric acid had a browner and darker tint. Indirubin was also present in these indigo preparations.

Whereas Schunck (*l.c.*) had described the production of various brown substances by the action of dilute acids on his indican, and Schunck and Roemer (*l.c.*) had obtained a brown-yellow compound by means of hydrochloric acid in absence of air, the behaviour of the pure crystalline glucoside in this respect was studied by Perkin and Bloxam. When 100 c.c. of a 4 p.c. solution of indican was treated with 3 c.c. of sulphuric acid, and digested at a boiling temperature, the liquid, at first yellow, became brown, a brown resinous substance, together with a little indigotin, quickly separated, and the presence of indole was observed. The product of the reaction was almost identical in weight with that required by the amount of indoxyl which the glucoside would yield on hydrolysis, and consisted chiefly of a dark reddish-brown powder (*a*), sparingly soluble in alcohol, together with a small quantity of a similar, though more readily soluble substance (*b*)[1] Analyses of (*a*), which is termed *indoxyl brown*, gave C=68·10; H=4·10; N=9·34, figures almost identical with those found by the same authors for the main constituent of indigo brown, and though these two products differed from one another in certain minor respects, there could be no doubt that they were closely allied. The more readily soluble substance (*b*) also closely resembled the indoxyl brown, and gave on analysis N=9·65 p.c. Indican, when treated with cold hydrochloric acid in the absence of air for 90 hours, gave indoxyl brown and a soluble brown substance similar to that described above (Perkin and Thomas). The acid filtrates from the indoxyl brown preparations contained dextrose, and this was identified by means of its osazone, and also by the preparation of its acetyl derivative.

The indigo enzyme discovered by Schunck (*l.c.*) has been elaborately investigated by the Dutch chemists. Beyerinck (Proc. K. Akad. Wetensch. Amsterdam, 1899, 1, 120) extracts the finely divided leaves of the plant, first with cold 96 p.c. alcohol, and subsequently with more dilute alcohol, which removes chlorophyll, indican, wax, &c., and leaves a snow-white highly active powder. From such preparations the enzyme itself could only be imperfectly removed, for in water it is almost insoluble, very sparingly so in glycerol, and rather more readily in 10 p.c. solutions of sodium and calcium chlorides respectively. The residue which remains after extraction in this way is not perceptibly less active than before treatment. A minute study of these leaf preparations was carried out by Beyerinck in regard to their behaviour with partly purified indican solutions, and he indicates the effect of temperature on the intensity of the hydrolysis by means of curves. Among numerous points of interest it was observed that ammonia quickly destroys the enzyme, and also that emulsin slowly hydrolyses indican, although the intensity of its action was only one-twentieth of that of *Indigofera* enzyme preparations.

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[1] According to Perkin (Chem. Soc. Trans. 1916, 109, 211) this operation can be so conducted that the total amount of nitrogen present in this product is approximately equivalent to that possessed by the indican originally employed.

Hazewinkel (*ibid.* 1900, 2, 513), who also investigated the subject in 1898, arrived independently at Beyerinck's conclusions. Finding that emulsin acted on indican solutions he called the indican enzyme *indimulsin*, and considered that a 10 p.c. solution of sodium chloride is the best medium for dissolving it. A very interesting point which he mentions is that during fermentation no indican passes from the leaf into the surrounding liquid.

In the paper of van Romburgh (*ibid.* 1899, 2, 344) allusion again is made to the insoluble character of the enzyme, and to the activity of emulsin with solutions of indican. Finally, Beyerinck (*ibid.* 1900, 3, 101) demonstrated that the ferment present in woad, *Isatis tinctoria*, is not capable of hydrolysing indican, though it reacts with isatan, the peculiar indigotin yielding principle of this plant. Bergtheil (Chem. Soc. Trans. 1904, 85, 877), whose paper covers ground already traversed by Hazewinkel, Beyerinck, and van Romburgh, considers that the difficulty which occurs in extracting the enzyme is due to the presence of tannin in the leaves (*cf.* Brown and Morris, Chem. Soc. Trans 1893, 63, 604). By pounding the leaves with hide powder the tannin becomes fixed, and a very active solution of the enzyme can be obtained.

Ter Meulen (Rec. trav. chim. 1905, 24, 444) is, however, in agreement with the other Dutch work referred to above, as is evident from his statement 'L'enzyme de l'indigo est insoluble dans l'eau.' According to Gaunt, Thomas, and Bloxam (*l.c.*). Bergtheil's product is not a true solution, as the enzyme is entirely removed from it by means of a Berkfeld filter. Thomas, Perkin, and Bloxam (Chem. Soc. Trans. 1909, 95, 829), again, point out that there is no certainty of the presence of tannin in the leaves of the *I. sumatrana* and *I. arrecta*, and that any tannin matter if originally present would be eliminated during the repeated extraction of the material with alcohol. As the result of their experiments the insolubility of the enzyme was confirmed.

A study of the hydrolysis of pure indican by means of the enzyme and subsequent oxidation of the indoxyl solution with air under varied conditions has been made by Thomas, Perkin, and Bloxam (*l.c.*). The fermentation was carried out in an atmosphere of purified hydrogen, and the temperature and dilution of the solution in both this and the subsequent oxidation process were so arranged as to fairly approximate the ordinary factory routine. For full details of apparatus and the analytical precautions adopted the original paper must be consulted.

The results of this investigation show that the hydrolytic action of the enzyme proceeds somewhat rapidly, and that by employing 2 grams of the enzyme and 1 gram of indican under the conditions of dilution stated, the reaction was complete after 2 hours' digestion at 50°. The solution, though free from indican, contains, however, less than the theoretical amount of indoxyl (93 p.c.). This is due to the fact that some quantity of the indoxyl (4 p.c.) is occluded by the enzyme powder, and it was found that by increasing the quantity of this latter a correspondingly greater loss occurs. The residual deficiency (3 p.c. approx.) arises from the instability of indoxyl itself, which even in an atmosphere of hydrogen at 50° is slowly converted into a product which is incapable of giving indigotin on oxidation. This property, which is referred to as the 'decay' of indoxyl, is much more evident when the digestion with the ferment is prolonged for several hours, and the experiments of these authors indicate that by such a treatment for 30 hours, at least 20 p.c. of the indoxyl undergoes this transformation. On the other hand, at 15°, in an atmosphere of hydrogen, the indoxyl solution is comparatively stable, and on standing for 24 hours, experienced a loss of only 3 p.c.

According to Beyerinck (*l.c.*) great attention should be paid to the degree of the acidity of indican solutions which are undergoing fermentation, and this is corroborated by Thomas, Perkin, and Bloxam. Thus, by the presence of a trace of sulphuric acid, during the fermentation, the decay of the indoxyl is practically inhibited, and, moreover, by the addition of a further quantity of the acid at the close of the operation, the occlusion of the indoxyl by the enzyme powder is also prevented. As a result of this procedure the solution contained 99·5 p.c. of the theoretical quantity of indoxyl.

When a dilute aqueous solution of indoxyl is oxidised by air the reaction is more complex than has usually been considered the case, and a quantitative yield of indigotin is not produced. Thomas, Perkin, and Bloxam have, for instance, found that the indoxyl solutions produced by the enzyme hydrolysis of indican, when treated with air at 60°, gave only 88 p.c. of the theoretical quantity of indigotin, admixed with a little indirubin. It thus appears evident that in addition to the oxidation of indoxyl to indigotin some secondary reaction occurs, but of the chemical nature of this change there is as yet no certain evidence. The isolation from the indigo thus produced of traces of substances resembling indoxyl brown or indigo brown indicates the effect, at least in part, of a condensation similar in character to that which is involved in the production of the former product. Moreover, the filtrate from the indigo, which is prepared in this manner, was invariably of a dull yellow colour, and yielded, by extraction with ether, a small quantity of a yellowish-brown resin.

This secondary change of indoxyl is facilitated by the presence of potassium acetate in the liquid during the oxidation, for by this means the yield of indigotin was decreased to 81 p.c., and the filtrate obtained from it possessed a rich dichromate colour. It has long been known that the oxidation of indoxyl solutions, in so far as the crude fermented factory liquid is concerned, is facilitated by the presence of ammonia or lime water, and the subject has been discussed by Rawson and by Beyerinck (*l.c.*). According to Thomas, Perkin, and Bloxam, the employment of a small quantity of either of these reagents during the oxidation of the indoxyl derived from pure indican was beneficial, and an increase of about 5 p.c. in the yield of indigo thus took place. On the other hand, the addition of only a trace of these compounds is advisable, because should an excess be present the amount of indigo produced is rather decreased than increased thereby.

But whilst both ammonia and lime water in suitable amount partially inhibit the secondary change of the indoxyl referred to above, a third factor, well known to manufacturers, comes into play, which is represented by the production of notable amounts of indirubin. For the formation of this colouring matter isatin is necessary, and it is likely that, in the presence of a large amount of the above reagents, an excessive production of this substance occurs, and occasions the decreased yield of indigo which, under these circumstances, has been shown to take place. It has, in fact, been pointed out by Perkin (Chem. Soc. Proc. 1907, 23, 30) that traces of isatin exist in Java indigos, which are rich in indirubin.

Curiously enough the presence of a trace of hydrochloric acid during the oxidation acts in the same manner as ammonia, though to a less extent, in increasing the yield of colouring matter, but in this case the reaction proceeds much less rapidly. The employment of pure oxygen with neutral solutions of indoxyl gives 3–4 p.c. less colouring matter than is obtained when air alone is employed, whereas in presence of ammonia the yield is but little affected. The addition of Chile saltpetre to the fermentation vat has been a custom of Indian planters for some time, and Rawson (Report on the Cultivation and Manufacture of Indigo, 2nd ed., 1907) states that although no increase of colouring matter is thus produced in the oxidation vat, the precipitate settles better. The laboratory experiments of Thomas, Bloxam, and Perkin with pure indican corroborate this statement. Finally, there is but little difference in the yield of colouring matter experienced when the solution of indoxyl is oxidised by air at either 30° or 60°, although, if anything, the advantage is in the case of the higher temperature.

As a result, therefore, of the employment of acid during the enzyme hydrolysis of indican, and oxidation of the resulting indoxyl solution under feebly alkaline conditions, the best yields of colouring matter have been obtained. On the other hand, it has not been found possible either with synthetical indoxyl or indoxyl derived from indican to obtain a quantitative yield of pure indigotin or of an admixture of this colouring matter with indirubin. In regard to the bearing of this work on the commercial process, Thomas, Perkin, and Bloxam suggest that the effect of the addition of a small quantity of sulphuric or oxalic acid to the fermentation vat should be studied. They consider, however, that the most satisfactory laboratory results on the preparation of indigotin from the plant extract, or from pure indican, are given when the solution is hydrolysed by hydrochloric acid, with simultaneous oxidation by air. The cost of hot water extraction of the plant is, however, considered by Rawson to be prohibitive.

Bacterial fermentation. Though in the manufacture of indigo, hydrolysis of the indican is mainly due to the action of its specific enzyme indimulsin, it is well known that the bacteria which are present exert a similar although minor effect.

In 1887 Alvarez (Compt. rend. 115, 286) isolated from an extract of the indigo plant, an organism *Bacillus indigogenus*, which was capable of producing this fermentation. Beyerinck (*l.c.*), who studied the matter in considerable detail, points out that a similar effect is produced by infecting indigo plant infusions with garden soil, and that in this case the common gas-producing bacteria perform the chief part. Alvarez, he suggests, went too far in insisting on the existence of a specific bacterium in indigo fermentation. On the other hand, Bergtheil (*l.c.*) considers that at least one organism capable of producing indigo fermentation is invariably found in large quantities in an infusion of the plant. This corresponds very closely with the description given by Alvarez of his *Bacillus indigogenus*, and is no doubt identical with it.

Manufacture of Indigo.

Water. Pure water in large quantity is necessary for the manufacture of natural indigo (Crookes, Handbook of Dyeing and Calico Printing, 1874; Indigo Manufacture, Bridges-Lee, 1892; Rawson, Report on the Cultivation and Manufacture of Indigo, 1902). When such is not available, Bridges-Lee recommends its purification, if hard, by treatment with lime water, and should much organic matter be present by the use of permanganate. Rawson also lays stress on this point, and recommends a similar method of procedure. In special circumstances the employment of alumino-ferric is advisable (Bergtheil, 1909). As the duration of the fermentation varies with the temperature of the water, Rawson recommends, in case this should be lower than 90°F., a preliminary heating in the reservoir.

Fermentation. The duration of this process is given by Crookes (*l.c.*) as 9–14 hours, according to the prevailing temperature of the water, whereas Georgievics (Der Indigo, 1892) suggests 18 hours when the external temperature is 35·6°C. In very hot weather the fermentation is completed in 6 hours. According to Rawson (*l.c.*) when the temperature of the fermentation vat is from 90° to 92°F. a 12 hours' steeping gives the best result in the case of the *I. sumatrana*; whereas Bergtheil (Indigo Research Station, Sirsiah, 1906) is of opinion that a 10 hours' fermentation is sufficient. With the *I. arrecta* the steeping should vary from 13 to 15 hours at 90°, according to the indican content of the plant. In other respects, according to Rawson and Bergtheil, there is practically no improvement necessary in the steeping operation as carried out in well-managed factories. The addition of such chemicals as mercuric chloride, sodium and potassium carbonates, lime, carbolic acid, formaldehyde, and sugar are not of advantage, although sodium nitrate, which has been employed by planters for many years past, may facilitate the deposition of the indigo in the oxidising vat. On the other hand, the work of Thomas, Bloxam, and Perkin indicates as beneficial the curtailment, as far as possible, of the steeping operation, and the addition of sulphuric or oxalic acid in small quantity to the vat as advantageous.

Hot-water extraction. The extraction of the indigo plant with hot water has been employed for many years, and in Bancroft's 'Philosophy of Permanent Colours' an account is given by Dr. Roxburgh, dated 1797, of such a method:—'The hot-water process begins to be used over these provinces . . . with it they can make indigo when the weather is too cold for the usual process of fermentation, and it gives a more beautiful and lighter indigo. . . . A more complete and certain extraction of the basis of indigo is effected by subjecting the plant to the action of water heated to about 150°–160°F.' Bridges-Lee (*l.c.*) claims an advantage by the employment of hot water, and heats the contents of the steeping vat gradually, either by direct fire or steam pipes. It is also well known that the Java planters who have employed the *I. arrecta* for several years past have favoured a hot-water process, and although the exact details of their methods have not been disclosed, it is certain that sulphuric acid is also employed in the manufacture. Perkin (Chem. Soc. Trans. 1907, 91, 435) refers to samples of Java indigo prepared by three distinct methods, viz. 'the new process with hot water,' 'the new process with cold water,' and 'the old process in which no chemicals are used.' There can be no doubt that by these hot-water processes the indican is very rapidly hydrolysed by the ferment, and that the indigo eventually produced is of a superior quality. During this hot extraction it appears preferable, as far as possible, to exclude air from the vat by means of a cover, and the necessity in this case is easy to understand because the evolution of carbon dioxide and other gases which act as a protection to the indoxyl during the ordinary process of fermentation, is greatly decreased when operating in this manner (Roxburgh, *l.c.*). Rawson (*l.c.*), who refers to a patent No. 157, 1892, granted to A. Schulte in Hofe, for manufacturing indigo on these lines, and also to Henly's 'heating process of 1888,' carried out numerous experiments on this subject with the *I. sumatrana*. In order to economise fuel the indigo plant was, in the first instance, extracted by the accumulative method; but, contrary to expectation, this did not give such good results as a simple extraction in ordinary vats fitted with perforated steam pipes. He finally concludes, however, that except in wet or cold weather the hot-water system offers no advantage over ordinary steeping carried out under favourable conditions. The indigo made by this method was, however, of better quality (75–77 p.c.) than that made in the ordinary way (50–55 p.c.). In regard to extraction of the plant by means of boiling water, or extraction by steaming, Rawson considers that the cost would be prohibitive.

When the fermented liquid is run into the oxidising vat, the residual plant still contains a small quantity of indoxyl. The question of a second steeping in order to recover this is referred to by Roxburgh as early as about 1797; he considers that a considerable economy would probably be effected thereby; but Rawson's (*l.c.*) experiments in this direction gave an unsuccessful result. Thomas, Perkin, and Bloxam (*l.c.*) suggest that the employment of a slightly acid water for this purpose should be advantageous, and that the amount of indoxyl retained by the plant residue is probably greater than the 5 p.c. (on the total colouring matter) believed by Rawson to be present. The extracted plant, known as 'seet,' is a valuable manure.

The oxidation vat. Although the oxidation of the fermented liquid was until very recently carried out to some extent by 'hand beating,' a method practised over a century ago, according to Bancroft (*l.c.*), this operation is commonly effected by machinery. The apparatus is identical with, or very similar to, the 'beating wheel,' a rimless wheel, the spokes of which are paddles, and which is now very generally employed in India. Geneste in 1888 patented the pumping in of air, and Bridges-Lee (*l.c.*) in 1891 a shower-bath arrangement, as improvements in the method of oxidation. Rawson, again (1902, Eng. Pat. 173), proposed to treat the liquid with acid and an alkaline persulphate; but although excellent results were obtained in the laboratory, these were not satisfactory on the manufacturing scale. As the outcome of an elaborate investigation, Rawson considers that the oxidation of the fermented liquid by blowers and compressors is superior to wheel beating, the yield being thereby increased about 20 p.c.

It has long been the custom to facilitate the deposition of the indigo by what were termed 'precipitants,' and experiments are recorded by Roxburgh, who employed for this purpose ammonia, stale urine, caustic lye, lime water, and potassium ferrocyanide. That such chemicals must be considered to have assisted in the more rapid oxidation of the indoxyl is certain, and their effect is not to be confused with the mere settlement of the indigo by the use of slaked lime, as adopted by the Chinese.

In 1894 Coventry patented a process which was based on the employment of lime under certain conditions. The invention consisted in the employment of a special vat intermediate between the steeping and oxidising vats, in which the fermented liquid was treated with lime. A copious precipitate of calcium and magnesium carbonates was thus produced, which on settling carried down various impurities. The supernatant liquid was then oxidised in the usual manner. The indigo thus produced is somewhat contaminated with lime, and the removal of this is subsequently effected by the addition of a certain amount of acid to the 'mal' in the boiler. Indigo prepared in this manner is of superior quality, and although not equal to the Java product resembles the latter in containing some quantity of indirubin. According to Rawson a substantially increased yield of colouring matter is given by this process.

Caustic soda added to indigo liquor before oxidising behaves very similarly to lime, and on the large scale gave an increase of 43 p.c. of dry indigo as weighed. Sodium peroxide also gave an average increase of 33 p.c., but on the whole was not so serviceable as caustic soda (Rawson).

The oxidation of the fermented plant extract in the presence of ammonia, first mentioned by Roxburgh (*l.c.*), was patented by Michea in 1876, whereas Geneste in 1889 suggested the use of caustic soda and ammonium sulphate instead of liquid ammonia itself. The use of ammonia is mentioned as beneficial by Georgievics (*l.c.*), and there appears to be no doubt that it is superior to the other reagents which have been employed for this purpose. In its presence the indoxyl is rapidly oxidised to indigotin, and the precipitated colouring matter settles well. The more general employment of ammonia in India has resulted from the work of Rawson, and its use in conjunction with the steam injector blower constitutes the most important improvement which he has recommended to the notice of the indigo planters. The procedure adopted by Rawson consists briefly in connecting the outlet of an ammonia still (containing lime and ammonium sulphate) loosely with the steam blower, so that when in action, ammonia, air, and steam are injected into the vat by means of perforated pipes laid at the bottom of the receptacle. During the operation the temperature rises 10°–15 F., and the oxidation is rapidly completed. The employment of ammonia gas and steam in connection with the beating wheel gives also satisfactory results. By these methods Rawson describes increases in the yields of dry indigo, varying from 37 to 63 8 p.c., and considers that the average increase of colouring matter is about 34 p.c. as compared with that given by the ordinary oxidising process.

On the other hand, Bergtheil (Report of the Indigo Research Station, Sirsiah, 1906, 6) states that the ammonia process effects very little, if any, improvement over ordinary oxidising when this is carried out under optimum conditions of speed, weather, &c.

After the indigo has settled in the vat, the supernatant liquid, or 'seeth' water, is run off as completely as possible. This seeth water, as a rule, contains more or less colouring matter in suspension, and it is during this operation that a considerable loss of indigo occurs, which may reach as much as 20 p.c. (Rawson). This, as a rule, is much reduced by using an alkali in oxidising, on account of the readier settlement of the precipitate. Rawson found that filter pressing cannot be employed for recovering the indigo, but suggests treating the 'seeth' water with an alkali which causes the suspended indigo to more readily subside. On the other hand, Bergtheil (1909) recommends the employment of alumino-ferric as an aid to the deposition of the indigo precipitate in the oxidation vat.

Davis (Agric. Res. Inst. Pusa, Indigo Publ. No. 3) recommends the use of Dhak gum to aid settling and to give a product which can be easily filtered and pressed. Loss due to incomplete settling is often considerable, and whereas alumino-ferric also precipitates impurities, Dhak gum has not this disadvantage. In certain cases Dhak gum, which is added five minutes before the beating is ended, gave an increase in yield of 70 p.c for Sumatrana working and of 35 p.c with Java plant. No appreciable deterioration of quality is observed. Not only does the addition of the gum give an increase in yield when the conditions for settling are bad, but again when these are good it causes no harmful effects.

Final treatment of indigo. According to Bancroft (*l.c.*) it was the practice of some manufacturers in the East Indies to purify their indigo by boiling it with water and fossil alkali (soda), whereas Roxburgh, as well as de Cosigny, recommended also the action of a diluted sulphuric acid. The more general procedure, until very recently, in India has consisted in merely boiling the semi-fluid indigo paste in a large cauldron, but the addition of dilute sulphuric acid appears now to be generally adopted. According to Rawson the quality of the indigo may be in this way improved 5–10 p.c. At the close of the operation the indigo is allowed to settle, the acid liquid run off, and the precipitate treated with fresh water and again boiled.

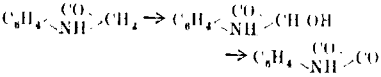
The subsequent filtering, pressing, and drying operations call for no special comment. The slow drying of the product appears to be most advantageous, and in this way an indigo of slightly higher percentage than when the mass is dried artificially is obtained. This is accounted for by the fact that certain impurities of the indigo in the presence of moisture undergo gradual decomposition with evolution of ammonia and other gases.

Briggs (Pat. Spec. 292, 1906) devised an apparatus for drying the indigo paste, and simultaneously converting it into powder. An illustration of this machine, essentially a revolving drum, appears in Bergtheil's Report, 1906, 12. Attempts, moreover, are being made to place natural indigo on the market in the paste form (*ibid.* 1910).

CONSTITUENTS OF NATURAL INDIGO.

In addition to indigotin, natural indigo contains varying proportions of indirubin, indigo brown, indigo gluten, and mineral matter. Indigo yellow or kaempferol is also present as a rule when the *I. arrecta* has been employed for the manufacture.

Indirubin. The identity of the natural indirubin or indigo red with the artificial product prepared according to Baeyer's method (*l.c.*), about which there was formerly some controversy, appears now to be fully established (Marchlewski and Radcliffe, J. Soc. Chem. Ind. 1898, 17, 434). Bloxam at one time (Chem. Soc. Trans. 1905, 87, 979) considered that a red substance other than indirubin was present in some quantity in natural indigo, whereas Bergtheil (Report of the Indigo Research Station, Sirsiah, 1906) has stated that 'decisively there is more than one red body in most commercial indigos.' The investigation of numerous samples of the dyestuff by Perkin and Bloxam (Chem. Soc. Trans. 1907, 91, 279, and 1910, 97, 1461) indicate, however, that this is not the case. Whereas certain varieties of natural indigo, notably Java and Coventry process indigos, contain notable amounts of indirubin, it is probable that a trace occurs in all samples of the natural dyestuff. That the indirubin originates from the indican existing in the leaves of the various species of *Indigofera*, and is due to no second constituent of the plant, is now certain, and its production is to be explained in all cases as due to the condensation of isatin with indoxyl. Thus it has been shown by Thomas, Bloxam, and Perkin (*l.c.*) that indigo containing indirubin can be readily produced from indican by a repetition of the factory method, and again, isatin itself has been isolated from natural indigo rich in indirubin (Perkin, Chem. Soc. Proc. 1907, 23, 30). The formation of the isatin is favoured by special circumstances such as the oxidation of the indoxyl by air in the presence of alkali or acid, and may also be affected to some extent by temperature. That indoxyl can be converted into isatin without an intermediate formation of indigotin has been shown by the Badische Anilin und Soda-Fabrik (D. R. P. 107719, 1898), and it has been found by Perkin (Chem. Soc. Trans. 1909, 85, 847) that indoxylic acid, on long standing in the presence of moist air, is converted chiefly into indirubin, although some quantity of indigotin together with a substance, probably indigo brown, and traces of isatin are simultaneously produced. Again, it has been pointed out (Thomas, Bloxam, and Perkin) that the indican present in air-dried leaves of the indigo plant slowly disappears, and, according to Perkin (private communication), this is accompanied in most cases by a development in the leaf of considerable quantities of indirubin. It appears probable that this so-called 'secondary' oxidation of the indoxyl proceeds according to the following scheme:—



$$C_6H_4\left<\begin{matrix}CO\\NH\end{matrix}\right>CH_2 \rightarrow C_6H_4\left<\begin{matrix}CO\\NH\end{matrix}\right>CH\cdot OH \rightarrow C_6H_4\left<\begin{matrix}CO\\NH\end{matrix}\right>CO$$

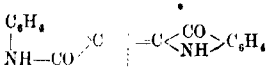
and may also be indirectly the cause of the production of indigo brown. The following are the results of analyses illustrating the percentages of indirubin and indigotin in certain indigos (Bloxam and Perkin):—

Java Indigo.—New process with hot water

Sample	Total colouring matter	Indigotin	Indirubin
1.	75·20	67·76	7·43
2.	73·60	63·86	9·51
6.	62·91	57·35	5·01
Java indigo.—New process with cold water			
7.	72·88	69·23	3·06
8.	71·02	66·35	4·04
9.	58·30	55·61	2·15
Java indigo.—Old process without chemicals.			
13.*	74·96	72·89	1·74
15.	69·51	68·26	0·99
Coventry process indigo.			
	61·76	56·63	5·23

Finally, Bloxam and Perkin refer to an abnormal sample of laboratory indigo prepared from pure indican, which contained 88·9 p.c. of colouring matter, and of this 25·83 p.c. consisted of indirubin.

Though indirubin was at one time considered to be a valuable constituent of natural indigo (*cf.* Rawson and Knecht, J. Soc. Dyers, 1888, 4 Hummel, *ibid.*; and Bergtheil, Report Indigo Research Station, Sirsiah, 1907, 7), it is now known that such is not the case. Fasal (Mitt. K. Tech. Gew.-Mus. Wien, 1895, 11, 307) found that the shade of colour given by an indirubin vat became bluer from day to day, and that this was due to the formation of indoxyl by the further reduction of the leuco-indirubin. More recently Perkin (Chem. Soc. Proc. 1909, 25, 127) has shown that in addition to indoxyl, *oxindole* is simultaneously produced, and this is in harmony with the formula assigned by Baeyer (*l.c.*) to this substance—



$$\begin{matrix}C_6H_4\\|\\NH—CO\end{matrix}>C=C\left<\begin{matrix}CO\\NH\end{matrix}\right>C_6H_4$$

In vat dyeing, therefore, indirubin may thus produce not more than one-half its weight of indigotin. Matthews (J. Soc. Chem. Ind. 1902, 21, 22), again, points out that indirubin requires for reduction a much stronger reagent than indigotin, and as a result, in practice, the greater part of this dyestuff is not attacked, but settles to the bottom of the vat.

On the other hand, indirubin disulphonic acid is, according to Fasal (*l.c.*) and also to Rawson and Knecht (*l.c.*), a useful dyestuff, and gives colours much faster to light than indigotin disulphonic acid, which is present as sodium salt in the 'indigo extract' of commerce.

Indigo brown. An important impurity of natural indigo is the so-called indigo brown, a product isolated and cursorily examined by both Chevreul (Gmelin, Handbook of Chem. 1859, 13, 48) and Berzelius (*ibid.*) In order to isolate this substance, the latter chemist digested indigo with boiling dilute sulphuric acid to remove indigo gluten, and subsequently with potassium hydroxide to dissolve the brown. The alkaline liquid was neutralised with acetic acid, evaporated to dryness, the residue digested with alcohol, and the solution evaporated. Thus obtained the indigo brown consisted of a dark-coloured resin, soluble in alkaline solutions. According to Schunck (Phil. Mag 1855, [iv.] 10, 74, and *ibid.* 1858, 15, 127) the indihumin $C_{10}H_9O_3N$, produced in conjunction with other brown amorphous products by the action of dilute acids on his indican, is perhaps identical with indigo brown.

Perkin and Bloxam (Chem. Soc. Trans. 1907, 91, 279) extracted Bengal indigo, which had been already digested with boiling dilute hydrochloric acid to remove the gluten, with boiling pyridine. In addition to a little indirubin the product contained three substances: (*a*) the main constituent $C_{16}H_{12}O_3N_2$ (?), insoluble in alcohol and acetic acid, (*b*) $C_{24}H_{22}O_5N_3$ (?), soluble in acetic acid, and (*c*) $C_{16}H_{14}O_4N_2$ (?), soluble in alcohol. These compounds, the molecular weight of which is uncertain, consist of brown amorphous powders, closely resembling one another in general property, and are readily reduced by zinc-dust in alkaline solution with formation of pale brown liquids. When digested with boiling 50 p.c. potassium hydroxide solution they give some quantity of *anthranilic acid*, a point which indicates that they are derived from indoxyl. At the same time a brown resinous substance is also produced, and this studied in the case of the main constituent (*a*) $C_{16}H_{12}O_3N_2$ contained $C=71·39$; $H=4·05$; $N=7·94$. Natural indigo further contains a small quantity of a brown substance, insoluble in pyridine, but soluble in boiling dilute alkali (Chem. Soc. Trans 1910, 97, 1473), and is distinguished from the compounds above enumerated by the fact that it is not susceptible to sulphonation (with 96 p.c. sulphuric acid) or conversion by this means into a product soluble in water. In the analytical method described by Rawson (J. Soc. Chem. Ind. 1899, 18, 251) this brown material, at least in part, consists of impurity which is carried down by a precipitation of barium sulphate in the liquid. There is now considerable evidence in favour of the view that the constituents of indigo brown are derived from indoxyl during the manufacture of indigo from the plant. The fact that indican itself, when boiled with dilute acids, produces the very similar indoxyl brown, and the isolation of brown substances, although in trifling amount, from indigo prepared by the hydrolysis of pure indican in the laboratory, harmonises with this suggestion.

Beyerinck (Proc. Roy. Akad. Scien. Amsterdam, 1899, 120) observed that the disappearance of indoxyl in a dyeing woad (*Isatis tinctoria*) leaf is accompanied by the appearance of brown substances Again, he states that 'strong acids, just as alkalis . . favour the formation of indigo from indoxyl, but then part of this substance constantly changes into a brownish-black matter.' It has also been noted by Thomas, Perkin, and Bloxam that the disappearance of indican in the leaves of the *I. sumatrana* on keeping is accompanied by the formation of brown extractive matter. Rawson, again (Report on the Cultivation and Manufacture of Indigo, Mozzufferpore, 1904), says, 'The blower . . by quickly getting rid of CO_2 gas . . . prevents decomposition of a portion of the colouring matter into worthless brown substances, which takes place to a greater extent under other conditions.' All indigos, moreover, appear to contain indigo brown, so that this property is irrespective of their origin, which may have been due to such distinct plants as the *Indigoferæ*, the *Polygonum tinctorium*, or the *Lonchocarpus cyanescens* of West Africa Finally, it has been shown by Perkin (*l c.*) that among the decomposition products of commercial indoxylic acid which has been kept for a long time, a brown compound exists, which has a very similar percentage composition, and is probably identical with the main constituent of indigo brown It is quite possible that indoxylic acid is produced during the fermentation process (Perkin) (*cf.* Ranking, *l.c.*), and may be concerned in the formation of this product. The percentage of indigo brown soluble in pyridine in natural indigos is very variable, and appears to depend upon the details of manufacture. Analyses made by Bloxam and Perkin (Chem. Soc. Trans. 1910, 97, 1472) gave the following result:—

Java indigo, new process, hot water.	*Java indigo, new process, cold water*	*Java indigo, ordinary process*	*Coventry process indigo.*	*New Bengal indigo*
5·4	5·2	4·15	8·7	9·60

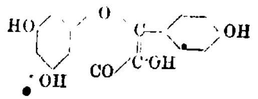
Except in the case of the Coventry process indigo, those samples had all been derived from the *I. arrecta.* The average amount of crude indigo brown—containing, however, some mineral matter—in numerous samples of Bengal indigo prepared from the *I. sumatrana* was 14 p.c. (Chem. Soc. Trans. 1907, 297).

Indigo brown dissolved in alkaline hydrosulphite solution does not colour cotton fabrics, though woollen material dyed with natural indigo and stripped by the method of Green, Gardner, Frank, and Lloyd (*l.c.*) frequently possesses a light brown tint which is probably due to the presence of this compound. The amount, however, remaining in this way on the fibre is not sufficient to materially strengthen the colour effect, and the frequently asserted superiority of the natural over the artificial variety of indigo can hardly therefore be accounted for in this manner.

Indigo gluten. Indigo gluten was first isolated from crude indigo by Berzelius (Berz. Jahresb. 7, 26), who extracted it with dilute acid, neutralised the extract with chalk, evaporated to dryness and dissolved out the gluten with alcohol. It was subsequently prepared by Orchardson, Wood, and Bloxam (J. Soc. Chem. Ind. 1907, 26, 4), who describe it as a horny mass, which on grinding gives a light biscuit-coloured powder, and when heated evolves ammonia In cake indigo it appears to exist in combination with mineral matter, possibly as a calcium compound, for though itself readily soluble in water, it can only be removed from the dyestuff by means of dilute mineral acid A considerable quantity of this substance is frequently present in indigo, and Perkin and Bloxam (*l.c.*) found that when the crude Bengal variety containing approximately 62 p.c. of indigotin was digested with dilute hydrochloric acid, it lost 21·5 p.c. of its weight. This figure naturally includes some quantity of mineral matter simultaneously removed by the acid. It has been suggested that this compound plays an important rôle in the dyeing operation, and accounts in part for the alleged superiority of natural over artificial indigo. This point, however, has not been scientifically investigated.

Indigo yellow. The first application of the term 'indigo yellow' to a substance existing in natural indigos is due to Bolley and Crinsoz (Jahres. 1866, 573), who state that it is to be found in the Bengal variety, and can be isolated by sublimation It is described as golden-yellow needles, subliming at 130°, and soluble in soda lye. Crude Bengal indigo, however, gives no sublimate of this character, (Perkin, Chem. Soc. Proc. 1906, 22, 198), but by submitting refined indigo, or the commercial synthetical variety to sublimation with limited access of air, a trace of a yellow compound $C_{15}H_8O_2N_2$ is produced. This substance, however, is insoluble in alkaline solutions and cannot, therefore, be the indigo yellow of Bolley and Crinsoz.

Rawson (J. Soc. Chem. Ind. 1899, 18, 251) detected in Java indigos a yellow compound, present usually to the extent of 2–3 p.c., although in one special sample as much as about 20 p.c. occurred. This substance was soluble in alkalis with a yellow colour; on heating it partially sublimed, and had the properties of an adjective yellow dyestuff. A more recent investigation (Perkin, Chem. Soc. Proc. 1904, 20, 172) has indicated that this in reality is *kaempferol*



a trihydroxyflavonol known to exist (Chem. Soc. Trans. 1902, 81, 587) in the flowers of the *Delphinium consolida* (Linn.) and other plants. Ultimately it was shown that the leaves of the *I. arrecta*, from which Java indigo is prepared, contain sometimes as much as 4 p.c. of a glucoside, *kaempferitrin* $C_{27}H_{30}O_{14}$, almost colourless needles, m.p. 201°-203°, which when digested with acid gives kaempferol and rhamnose

$$C_{27}H_{30}O_{14}+4H_2O=C_{15}H_{10}O_6+2C_6H_{12}O_5,H_2O$$

This compound is not hydrolysed by the indigo enzyme, and no enzyme has as yet been isolated from the plant possessing such a property. It is likely (Chem. Soc. Trans. 1907, 91, 435) that the use of sulphuric acid, when manufacturing Java indigo, may result in the contamination of the dyestuff with kaempferol. When the wet indigo sludge or 'mal' is boiled in the 'mal' boiler with addition of a little of the acid, the kaempferitrin present in the adhering water will be hydrolysed, and the insoluble colouring matter remain with the indigo. Samples of Java indigo more recently obtained contained only a trace (0·2 p.c. approx.) of kaempferol, whereas in a sample of the new Bengal indigo manufactured from the *I. arrecta* approximately the same quantity was detected (Perkin, private communication). If indigo mixed with kaempferol is cautiously sublimed the sublimate then contains appreciable quantities of this yellow colouring matter, and it seems likely, therefore, that this is in reality the indigo yellow of Bolley and Crinsoz, but that the indigo experimented with by these authors did not, as they supposed, originate from Bengal. The leaves of the *I. sumatrana*, the Indian indigo plant, contain but the merest trace of a yellow dyestuff resembling kaempferol, but according to Henry (Gmelin's Handbook of Chem. 1846, 13, 50) the *Polygonum tinctorium*, or Chinese indigo plant, contains appreciable quantities of a yellow colouring matter.

SEETH WATER.

When 'seeth' water, the liquid from which the indigo precipitate settles out at the conclusion of the oxidation process, is evaporated to dryness, yellowish-brown to deep brown residues are obtained. These products are extremely hygroscopic and when ground emit an odour resembling that of decayed cheese. Three samples of this material were examined by Perkin (Chem. Soc. Trans. 1916, 109, 211), the first and most important of which, derived from water drawn from an oxidation vat in the Purtabphore factory in India, represented 0·75 p.c. of the original liquid. As in the process of manufacture 100 parts of *I. sumatrana* underwent fermentation in the presence of 540 parts of water, this residue corresponded to 4 p.c. of the original plant. Sample (*b*) consisted of evaporated drainings from the mahl table of the same factory and formed 0·77 p.c. of the original liquid, whereas the origin of sample (*c*) was doubtful.

The samples were neutral, in the main dissolved readily in water, and these liquids on acidification emitted a strong odour of volatile aliphatic acids. When incinerated, all yielded considerable amounts of mineral matter which consisted mainly of the oxides of calcium magnesium and potassium, traces of manganese oxide and alumina being also present.

When agitated with boiling water, a small amount of an insoluble brown precipitate separated which in appearance closely resembled indigo brown, and was found to consist of a mixture of compounds of variable nitrogen content. The main constituent isolated as a dark brown amorphous powder, gave on analysis C=65·70; H=5·07; N=8·03 p.c., figures somewhat lower than those found for the main constituent of indigo brown (*l.c.*), whereas the more soluble fraction again contained still more oxygen C=64·7; H=5·0; N=4·6. From the neutral filtrate a small amount of succinic acid was isolated, the main bulk, approximately 20 p.c. of the 'seeth' water residue, consisting of a protein-like compound (N=8·22) which on heating evolved ammonia and in general property resembled the so-called 'indigo gluten' of crude indigo. It consisted of a friable mass, and to the presence of this substance the very hygroscopic nature of the dried 'seeth' residue was evidently due.

The following table illustrates the main results obtained by the analysis of the three samples of 'seeth' water residue:—

	(*a*) Per cent.	(*b*) Per cent	(*c*) Per cent.
Nitrogen . .	2·25	2·77	2·72
Ash . . .	27·30	25·90	26·87
Volatile acids .	23·80	21·04	—
Succinic acid . .	2·21	2·18	—
Brown matter .	5·58	12·03	11·18
Indigotin . .	0·18	0·10	0·082

THE ANALYSIS OF INDIGO.

The methods which have been proposed for the analysis of indigo are of a varied character, and the literature upon the subject is extremely voluminous.

These may be classified as follows: methods (*a*) involving the extraction of impurities with volatile solvents (Schutzenberger, Die Farbstoffe, ii. 526); (*b*) the extraction of indigotin with coal-tar oil (Stein, Die Prufing der Zeugfarben); with aniline (Honig. Zeitsch. angew. Chem. 1899, 280); with phenol (Brandt, J. Soc. Dyers, 1898, 34); with naphthalene (Schneider, *ibid.* 1895, 194); with nitrobenzene (Gerland, J. Soc. Chem. Ind. 1897, 108); with acetosulphuric acid (Möhlau and Zimmermann, Zeitsch. farb. text. Chem. 1903, 10, 189); (*c*) the extraction of indigotin by sublimation (Lee, Chem. News, 1884); (*d*) the extraction of indigotin by processes of reduction, lime, and ferrous sulphate (Berzelius), stannous chloride and caustic soda (Dana, Jahres. f. prakt. Chem. 26, 398), zinc and caustic soda (Owen, Amer. Chem. J. 10, 178), grape sugar, alcohol and alkali (Fritzsche, Dingl. poly. J. 1842, 86, 306), and hydrosulphite and lime (Rawson, *l.c.*); (*e*) estimation of nitrogen (Voeller, Zeitsch. angew. Chem. 1891, 110).

More important, however, are the methods based upon the titration of a solution of the sulphonated indigo by oxidising agents (*f*) chlorine water (Berzelius), chloride of lime (Chevreul, Leçons d. chem. appliq. de la teinture, ii.), potassium chlorate and hydrochloric acid (Bolley, Dingl. poly. J. 119, 114), potassium dichromate and hydrochloric acid (J. pr. Chem. 1851, 18, and Schlumberger, Bull. de la Soc. Mullhouse, 1863, 210, 284), potassium dichromate and oxalic acid (Kinley, Chem. News, 1863, 210, 284), potassium ferricyanide (Ullgren, Annalen, 136, 96), and potassium permanganate (Mohr, Dingl. poly. J. 132, 363); and by reducing agents (*g*) sodium hydrosulphite (Müller, Ber. 1880, 13, 2283), and titanous chloride (Knecht, J. Soc. Dyers, 1904, 97, and *ibid.* 1905, 292).

Finally (*h*) colorimetric methods (Dingl. poly. J. 27, 54, and 40, 448); (*i*) spectrum analysis (Wolff, Zeitsch. anal. Chem. 17, 65, and *ibid.* 23, 92); and (*k*) dye trial methods (Chevreul, *l.c.*, and Grossmann, J. Soc. Dyers, 1897, 124) have been proposed.

Of these methods of indigo analysis, modifications of Mohr's permanganate process are most generally employed, although others involving the reduction of sulphonated indigo with titanous chloride and sodium hydrosulphite are to some extent in use.

The permanganate methods. In order to eliminate the error due to the oxidising action of permanganate upon substances other than indigotin which are present in natural indigo, Rawson, who has been the pioneer in this respect, has devised two processes.

Salting-out method. 0·5 gram of finely powdered indigo mixed with its own weight of ground glass is sulphonated in a porcelain crucible by means of 20 c.c. of concentrated sulphuric acid at 70° for ¾ 1 hour; the product is diluted with water to 500 c.c. and the liquid filtered to remove insoluble impurities. 50 c.c. of this solution are mixed with 50 c.c. of water and 32 grams of common salt, and after standing for 1 hour the precipitated sodium indigotin sulphonate is collected and freed from certain soluble impurities by washing with about 50 c.c. of salt solution (sp.gr. 1·2). The precipitate is dissolved in hot water, treated with 1 c.c. of sulphuric acid, diluted to 300 c.c., and titrated with a solution of *N*/50 potassium permanganate. The liquid gradually takes a greenish tint, and the final disappearance of this constitutes the end point of the reaction. According to Rawson, 1 c.c. of the *N*/50 permanganate corresponds to 0·0015 of pure indigotin (J. Soc. Dyers, 1885, 74 and 201; A Manual of Dyeing, Knecht, Rawson, and Löwenthal, 1910, 817). Such a factor, however, according to Bloxam (*l.c.*) gives too high figures even with pure indigotin, and this has been corroborated by Frank and Lloyd (*ibid.* 1913, 226), who consider 0·00147 as more correct, and with this Rawson (*ibid.* 1914, 21) is now in agreement.

Barium chloride precipitation process. 0·5 gram of indigo is sulphonated as before, and after diluting with water, but before making up to 500 c.c., 10 c.c. of a 20 p.c. solution of barium chloride are added. The barium sulphate formed carries down with it the suspended impurities of the indigo, and the clear liquid can be pipetted off and titrated as before. The results are practically identical with those given by the 'salting-out' method (Rawson, J. Soc. Chem. Ind. 1899, 251).

Bloxam (*ibid.* 1906, 735) notes that the barium precipitate thus produced is always coloured blue, and this is confirmed by Bergtheil and Briggs (*ibid.* 1906, 729). The latter authors contend that the results given by this modification of Rawson are therefore too low, and consider that this defect is obviated by adding instead of barium chloride, freshly precipitated barium sulphate to the indigo mixture.

Grossmann (*ibid.* 1905, 308) throws down the impurities from the indigo solution with calcium carbonate. Bergtheil and Briggs (*l.c.*) and also Bloxam (*l.c.*) find that some quantity of the colouring matter is also precipitated in this way. Knecht, however, recommends its successful use even in larger quantity (J. Soc. Dyers, 1904, 97, and 1905, 292) in connection with his titanous chloride method; but Bloxam (*l.c.*) points out that such being the case this can only be due to the observance of conditions which are not stated in Knecht's paper.

Hydrosulphite method. This process, devised by Müller (Ber. 1880, 13, 2283), depends upon the fact that sodium hydrosulphite ($Na_2S_2O_4$) quantitatively reduces pure indigotin sulphonic acids to their corresponding leuco compounds. The solution of the hydrosulphite contained in a stone bottle is covered with a layer of petroleum to prevent oxidation and connected with a supply of hydrogen gas. By means of a siphon, or other convenient arrangement, the liquid can be drawn into a burette. The solution should be equivalent to about 1 c.c. = 0·0025 gram of indigotin, and the titrations are performed in an atmosphere of hydrogen or coal gas.

Titanous chloride method. This reagent is much more stable than sodium hydrosulphite, and Knecht (J. Soc. Dyers, 1904, 97, and 1905, 292) was the first to recommend its use for the analysis of indigo. The apparatus employed is similar in character to that required for the hydrosulphite process, and the titration is carried out in an atmosphere of carbon dioxide. If the reduction of the indigotin is effected by the titanium chloride in the presence of mineral acid, no definite end-point can be observed (Knecht), but by the addition of salts of tartaric acid this end-point is rendered quite definite.

In working with natural indigo, Knecht (Manual of Dyeing; Knecht, Rawson, and Löwenthal, 822) sulphonates 1 gram of indigo with 5 c.c. of 100 p.c. sulphuric acid at 90° for 1 hour. The solution diluted to 300 c.c. is warmed and slowly treated with 12 grams of chalk, cooled, made up to 500 c.c., and 50 c.c. of the clear liquid, to which 25 c.c. of a 20 p.c. solution of Rochelle salt has been added, is titrated whilst boiling with titanium chloride.

On account of the sparing solubility of Rochelle salt, Bloxam (*l.c.*) recommends the use of sodium tartrate, but states that the presence of excess of this or of Rochelle salt (as advocated by Knecht) is to be avoided, or otherwise too high percentages of indigotin are indicated. In the case of pure indigotin (1 gram) sulphonated with 20 c.c. of 100 p.c. sulphuric acid, and made up to 500 c.c. with water, 25 c.c. of this liquid (containing 1 c.c. of acid) requires 4 grams of the sodium tartrate to give quantitative results when titrated with a solution of titanium chloride containing 1 c.c. of concentrated hydrochloric acid per 50 c.c. of solution.

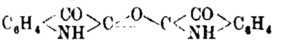
Bloxam (Chem. Soc. Trans. 1905, 87, 975; J. Soc. Chem. Ind. 1906, 25, 735), Orchardson, Wood, and Bloxam (*ibid.* 1907, 26, 4), and Gaunt, Thomas, and Bloxam (*ibid.* 1907, 26, 1174) have critically investigated the subject of indigo analysis. Among the methods for preparation of pure indigotin, that involving the crystallisation of crude material from nitrobenzene was discarded as untrustworthy, but the elaborate process of the B.A.S.F. Co. (Brochure, 1900) was found to give a pure substance. On the other hand, sublimation under reduced pressure in Jena flasks immersed in fusible metal at 370°-390°, gave, with synthetical indigo of 92 p.c. (approx.), a beautifully crystalline substance, which, after washing with boiling acetic acid, followed by boiling alcohol, was usually chemically pure. The permanganate factor resulting from experiments with these specially purified materials was 1 c.c. of permanganate solution 1/1000 0·00222 gram indigotin solution 1/5000, and is in agreement with that previously adopted by the B.A.S.F. Co. Wangerin and Vorlander (Zeitsch. Farben und Textilchemie, 1902, 1, 281) have stated that indigotin suffers loss of strength by oxidation, even when it is sulphonated by 94 p.c. sulphuric acid at 95°-100° for half an hour, whereas 8 p.c. fuming acid gives a deterioration of from 2 to 14·2 p.c., according to the time of heating. With the indigotin, however, purified as above, Bloxam showed that heating with 20 p.c. fuming acid for ¾ of an hour at 97° gave no loss, whereas with 30 p.c. acid for 20 minutes at 97°, a deterioration of only 1 p.c. could be observed. In both these cases indigotin tetrasulphonic acid was produced.

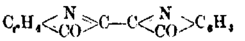
The tetrasulphonate method. As a result of these experiments a method for the analysis of indigo based on sulphonation with fuming acid was devised. 1 gram of the indigo, and 2-3 grams of purified sand (powdered glass contains iron, and should not be employed) is treated with 5 c.c. of 25 p.c. fuming sulphuric acid for half an hour in the water oven, and the solution is made up to 500 c.c. with water. 100 c.c. of this solution is treated with 100 c.c. of potassium acetate solution (450 grams per litre) which causes the precipitation of indigotin tetrasulphonate. The mixture is now warmed, and on cooling finally in ice-water,[1] the salt completely separates in a crystalline condition. This is collected by means of the pump on a Gooch crucible, and washed free from the brown supernatant liquid with a solution containing 90 grams of potassium acetate and 5 c.c. of acetic acid in 600 c.c. of water. The product is dissolved in 200 c.c. of water, and 20 c.c. of this solution, diluted with 80 c.c. of water, is treated with 0·5 c.c. of sulphuric acid, and titrated with permanganate (1/1000). In order to verify the accuracy of this method, Orchardson, Wood, and Bloxam studied the behaviour of indigo brown and indigo gluten, the main impurities of indigo, when submitted to the analytical process, as this subject had not been investigated by previous workers. Indigo brown when sulphonated with 96 p.c. acid gives, when dissolved in water, a dark-brown liquid, which is attacked by permanganate, though not perhaps so readily as the indigotin sulphonic acids, whereas indigo gluten gives similarly a light yellow solution, which is very rapidly oxidised by the reagent. On the other hand, kaempferol or indigotin yellow, treated in the same manner, gave a product which most readily absorbs permanganate, and, indeed, Rawson (J. Soc. Chem. Ind. 1899, 251) had already pointed out its deleterious effect in indigo analyses. Finally, these authors prepared and submitted to analysis by Bloxam's process mixtures containing known quantities of indigotin and one or other of all of these impurities, with the result that the colouring matter was thus estimated with considerable exactness. Bloxam (Chem. Soc. Trans. 1910, 97, 1473), by an adaptation of the pyridine method for the estimation of indirubin (*l.c.*), in which the impurities are eliminated by a process of extraction, has analysed natural indigos, and obtained the same figures as those given by the tetrasulphonate method. Again, by Knecht's titanium chloride method, and employing the modifications above described, this process can also be effectively worked. It is only reasonable to suppose that an analysis based on the selective precipitation of the sulphonated colouring matter is more likely to be efficient than that which presumes the deposition of varied impurities of a diverse chemical character by one specific reagent, and the somewhat lower results given by the tetrasulphonate method, as distinguished from those yielded by the processes previously in use, are in reality due to the almost complete elimination of these impurities from the indigotin sulphonic acid during the analysis. Rawson (*l.c.*) is, however, of opinion that the effect of these impurities on the analytical results has been much overrated; but, on the other hand, no experimental evidence is given in support of this view (Manual of Dyeing, *l.c.*, 818).

The action of potassium permanganate on solutions of the indigotin sulphonic acids is of interest, because the amount of the reagent necessary for the decolorisation of the liquid varies to some extent with the concentration (Rawson, A Dictionary of Dyes, Mordants, &c., by Rawson, Gardner, and Laycock, 1901, 187). At the concentrations employed by the B.A.S.F. Co., and adopted by Bloxam (*l.c.*), 1 gram of indigotin as sulphonic acid requires 0·45 gram of permanganate for decolorisation, whereas the equation

$$5C_{16}H_{10}O_2N_2+4KMnO_4+6H_2SO_4$$
$$=10C_8H_5O_2N+2K_2SO_4+4MnSO_4+6H_2O$$

implies that 0·4824 gram of the reagent is necessary. Again, for the oxidation under similar conditions of indirubin sulphonic acid considerably less permanganate is required, although the oxidation in this case is of a slower character. Bloxam and Perkin (Chem. Soc. Trans. 1910, 97, 1462) consider, therefore, that the oxidation is of a complex nature, and consists either (*a*) of two distinct stages in the formation of isatin sulphonic acid, or (*b*) of two distinct reactions involving the production of two separate substances. According to the first suggestion the isatin sulphonic acid formation would be preceded by that of an intermediate compound (I.), whereas by the latter, in addition to isatin sulphonic acid, a dehydroindigotin sulphonic acid (II.) may be produced—

I. 
$$C_6H_4{<}{}^{CO}_{NH}{>}C{-}O{-}C{<}{}^{CO}_{NH}{>}C_6H_4$$

II. 
$$C_6H_4{<}{}^{N}_{CO}{>}C{-}C{<}{}^{N}_{CO}{>}C_6H_4$$

In case the first product of the reaction consists entirely of dehydroindigotin sulphonic

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[1] Prolonged heating should be here avoided, and it is preferable that the solution of the tetrasulphonate with its subsequent recrystallisation should be effected without unnecessary delay.

Annalen, 136, 96), and potassium permanganate (Mohr, Dingl. poly. J. 132, 363); and by reducing agents (*g*) sodium hydrosulphite (Müller, Ber. 1880, 13, 2283), and titanous chloride (Knecht, J. Soc. Dyers, 1904, 97, and *ibid.* 1905, 292).

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Extraction with pyridine. Bloxam and Perkin (Chem. Soc. Trans. 1900, 97, 1460) find, as the result of experiments on mixtures of indigotin and indirubin, that neither commercial ether nor acetone are reliable solvents for the complete extraction of indirubin, and that their action, especially in the former case, is chiefly due to the presence of alcohol. Whereas acetic acid is efficient in this respect, and Koppeschaar's process gives approximately good results, pyridine is a much better solvent, and a method for the complete analysis of indigos containing indirubin based on the application of this liquid is described by these authors.

The indigo (0·25–1 gram) evenly incorporated with purified sand (20–30 grams) is introduced into a thin-walled glass tube, termed the 'container,' closed at one end by means of cotton cloth, on which has been placed a layer of asbestos and purified sand or of sand alone. Sufficient sand is then added to form a layer on the surface of the indigo mixture, which is then covered with asbestos, and the container is now placed in a Soxhlet tube and extracted with boiling pyridine. The extract is distilled down to a small bulk, the residue treated with boiling water and again distilled, and this operation is repeated until the last traces of pyridine have disappeared. The precipitate, which consists of indirubin together with a little indigotin and indigo brown, is collected, freed from the latter by means of dilute alkali, and the residue is sulphonated with 5 c.c. of sulphuric acid at 100°. The product is dissolved in water, filtered, and the amounts of indigotin and indirubin present ascertained by means of the Duboscq tintometer.

The residue in the container is percolated with water, followed with boiling dilute hydrochloric acid to remove indigo gluten, and is now introduced into a beaker and dried. The colouring matter present is sulphonated with 20 c.c. of sulphuric acid in the usual way, the product after dilution is filtered, and the solution of the indigotin sulphonic acid is estimated with permanganate, employing the directions given by Bloxam (*l.c.*). Analyses of mixtures of pure indigotin and indirubin, and also of commercial indigos, are given in the paper, and it is also pointed out that by this method an approximate estimation of the indigo brown present in the latter can be carried out.

THE ESTIMATION OF INDICAN IN THE LEAVES OF INDIGO PLANTS.

Although some indication of the indigo-yielding capacity of the plant can be obtained by ordinary steeping experiments, this method was found by Rawson (Cultivation and Manufacture of Indigo, *l.c.*) to possess several drawbacks, and numerous experiments were therefore carried out by him on the quantitative formation of indigo from the leaf extract by the simultaneous action of acids and oxidising agents. As regards the latter, ferric chloride, potassium chlorate, and hydrogen peroxide were tried, but persulphuric acid gave much the best results.

Persulphate method. 20 grams of leaves are extracted for 2 minutes with 250 c.c. of boiling water, the solution is strained through muslin, and the residues squeezed and washed with boiling water. The solution is treated with 5 c.c. of 20 p.c. hydrochloric acid, and 40 c.c. of a 5 p.c. solution of ammonium persulphate. The persulphate is not added all at once; at first 2 c.c. are added, after half an hour 2 c.c. more, and again 2 c.c. after another half an hour. After 2 hours the remainder of the ammonium persulphate is added, and when the mixture has stood for a further period of an hour, the indigo is collected and estimated by permanganate in the usual manner. Bergtheil and Briggs (J. Soc. Chem. Ind. 1906, 734) point out, however, that this process of Rawson's requires modification, as the addition of the reagents at such a high temperature involves a loss of indigotin. The main features of a modification of the process devised by these latter authors are the addition of acid to the cooled extract, and a determination of the course of the reaction, after addition of small amounts of persulphate, by filtration of a portion of the mixture and the addition to the filtrate of a trace of the oxidising agent.

Orchardson, Wood, and Bloxam (*ibid.* 1907, 40; *cf.* also Bloxam and Leake, Research Work on Indigo, Dalsingh, Serai, 1905), who employ sulphuric acid and persulphate, arrived independently at the same conclusion. To 200 c.c. of the leaf extracts these authors add 100 c.c. of a mixture of equal parts of 2 p.c. ammonium persulphate, and 4 p.c. sulphuric acid, and the mixture is kept at 60° for one hour. A comparison of their methods with that of Bergtheil and Briggs indicated an identical result in each case, and an increase of 20–25 p.c. of pure colouring matter in comparison with that yielded by Rawson's original process.

The isatin method. Beyerinck (Proc. K. Akad. Wetensch. 1899, 120), in discussing indican, suggested the possibility that by warming its solution with isatin and acid a quantitative yield of indirubin might be produced. Orchardson, Wood, and Bloxam (*l.c.*) have employed this reaction for the estimation of the leaf, and have devised the following method for this purpose:—

250 c.c. of extract, equivalent to 5 grams of the leaf, is treated with 0·1 gram of isatin, and the mixture boiled for 5 minutes to expel air, carbon dioxide being passed through the flask. 20 c.c. of hydrochloric acid is then added by means of a tap funnel, and the whole kept boiling for 30 minutes. The precipitate is collected on a tared filter, washed with hot 1 p.c. soda to remove brown compounds, then with 4 p.c. acetic acid and dried. An aliquot portion of the crystalline product is sulphonated, and analysed by the titanous chloride method, adopting the modifications employed by Bloxam (*l.c.*). The indirubin thus obtained is usually almost pure (98·5 p.c.), so that for an approximate estimation the latter part of the process is unnecessary. Gaunt, Thomas, and Bloxam (*ibid.* 1907, 26, 56) have examined the process in greater detail, and point out that by its employment pure indican gives quantitative figures (*cf.* also Perkin and Bloxam, Chem. Soc. Trans. 1907, 91, 90). On the other hand, this method gives considerably higher figures, both with pure indican (15 p.c.) and the leaf extract (25 p.c.), than those which are obtained by the persulphate process (Orchardson, Wood, and Bloxam; and Gaunt, Thomas, and Bloxam, *l.c.*). The unsatisfactory figures

in the latter cases arise from a further oxidation of the indigo by the persulphate. That this isatin method does not appear to be affected by other plant constituents was shown by the successful estimation of indican, purposely added to an extract of the leaves of the *Tephrosia purpurea* (Pers.), a plant in which this glucoside is absent.

EFFICIENCY OF THE PROCESS.

The actual yield of indigotin from the plant during the manufacture is not discussed by Rawson (*l.c.*), but this author considers that if the suggestions enumerated in his report are adopted, there is little or no room for a remunerative alteration of the process. Bergtheil, on the other hand, considers that under the conditions he describes (1906, 12) the efficiency is represented by an 82 p.c. yield, or that if to this be added the 5 p.c. believed by Rawson to be retained by the extracted plant, 87 p.c. is thus accounted for. The quantity of indigo estimated refers to the precipitate present in the vat after oxidation, and from this must be, therefore, deducted the indigo (10-20 p.c.) lost by the 'running off' of the 'seeth' water, so that the actual yield of dry colouring matter may thus represent from 62 to 72 p.c. of the theoretical quantity. Recent experiments, however, indicate that by adding aluminoferric to the oxidation a more perfect settlement of the indigo is to be anticipated (*ibid.* 1909).

Bloxam (Dalsingh Serai Report, and J. Soc. Chem. Ind. 1906, 25, 735), who examined the daily output of indigo (as pressed cake) from the Pembarandah factory, found that the first cuttings of the plant (Moorhun mahai) represented an approximate value of 0·1495 p.c. of indigotin from the plant, whereas the second cuttings gave a value of but 0·1526. Assigning to the plant the low value of 0·3 p.c., a considerable and serious loss is thus apparent. Moreover, the estimation of the results given by the 'isatin' method of leaf estimation, and of the finished cake by the 'tetrasulphonate' process (*l.c.*), both of which have been standardised with extreme care, point to a loss during the manufacture much greater than has hitherto been acknowledged (Report to Government of India, 1908).

Apart from the retention of indoxyl by the residual plant in the steeping vat, and the mechanical carrying over of indigo by the 'seeth' water, the deficiency of colouring matter is chiefly to be attributed to the conversion of indoxyl into products other than indigotin. Rawson (*l.c.*) has pointed out that if the fermented liquid is allowed to stand before oxidation a considerably decreased yield of indigo is ultimately observed. Thus, on the large scale, by standing for 6 hours a loss of 16·1 p.c. was apparent. Perkin and Bloxam (*l.c.*) have found as a result of their experiments with pure indican, that this alteration or 'decay' of indoxyl takes place not only in this manner during the fermentation process, but they consider that the indoxyl from the moment of its production by the hydrolysis of indican until its final conversion into indigotin is continually suffering this alteration. This peculiar reaction is, according to these authors, considerably inhibited by the presence of acid.

COMMERCIAL NATURAL INDIGOS.

When natural indigo was at its zenith very numerous varieties of this dyestuff were placed on the market, but more recently, owing to its severe competition with the artificial colouring matter, many of these are now rarely met with. From Asia came the indigos of Bengal, Oudh, Madras, Java, Manilla; from Africa those of Egypt and Senegal; and from America those of Guatemala, Caracas, Mexico, Brazil, South Carolina, and the Antilles.

The best varieties are the Bengal, Java, and Guatemala, although in England the Bengal is now mainly employed. Java indigo, formerly largely esteemed for the manufacture of indigo extract, chiefly because of its general purity, at the present time appears to find its market chiefly in the East.

A good quality of natural indigo has a deep violet-blue colour; it acquires a coppery lustre when rubbed with the finger-nail; it is light, porous, adhering to the tongue, and can be readily broken and ground. Low qualities, which contain much extractive and mineral matter, are dull and greyish in appearance, heavy, tough, and hard, and do not become bronzy by rubbing with the finger-nail.

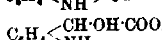
THE PROPERTIES AND SYNTHESES OF INDIGOTIN.

The history of the determination of the constitution of indigotin and of the many syntheses which have been devised for its preparation, leading as they have done to the successful manufacture of the artificial product, constitutes without doubt one of the most interesting chapters in the annals of synthetical organic chemistry. This has been dealt with so fully in other manuals that a brief résumé of the main features of the subject will only be given here, and to avoid detail the main reactions are only expressed by constitutional formulæ.

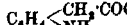
Whereas early work had proved the benzenoid character of indigotin, by the production from it of aniline, anthranilic acid, picric acid and nitrosalicylic acid and isatin, the commencement of a systematic attack on the problem of its structure first dates from the work of Baeyer and Knop (Annalen, 1865, 141, 1).

That isatin $C_8H_5NO_2$ was simply related to indigotin, at that time expressed as C_8H_5NO, appeared probable, and with the hope of reconverting isatin into the latter, its behaviour on reduction was studied by these chemists. The results obtained, though unsuccessful at first in their immediate object, proved to be of considerable importance, and indeed form the basis from which much of our present knowledge of the subject has been derived.

When reduced isatin gives dioxindol (I.), oxindol (II.), and these substances are now known to respectively consist of the inner anhydrides of *o*-amino-phenylglycollic (III.) and *o*-amino-phenylacetic acids (IV.)—

I. 

$$C_6H_4\left<\begin{matrix}CH\cdot OH\\ NH\end{matrix}\right>CO$$

II. 

$$C_6H_4\left<\begin{matrix}CH_2\\ NH\end{matrix}\right>CO$$

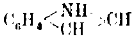
III.

$$C_6H_4\left<\begin{matrix}CH\cdot OH\cdot COOH\\ NH_2\end{matrix}\right.$$

IV.

$$C_6H_4\left<\begin{matrix}CH_2\cdot COOH\\ NH_2\end{matrix}\right.$$

By further reduction indole is obtained, and to this, which was subsequently synthesised by Baeyer and Emmerling (Ber. 1869, 2, 680), by fusing *o*-nitro-cinnamic acid with potash and iron filings the formula

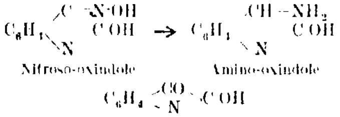


$$C_6H_4{<}\substack{NH\\CH}{>}CH$$

was assigned (Ber. 1870, 3, 517).

The same chemists again by heating isatin with phosphorus oxychloride and acetyl chloride under pressure obtained indigotin.

In 1879 Baeyer and Suida (Ber. 1878, 11, 584) converted oxindole into isatin according to the following scheme:—



$$C_6H_4{<}\substack{C-N\cdot OH\\N}{>}C\,OH \rightarrow C_6H_4{<}\substack{CH-NH_2\\N}{>}C\,OH$$

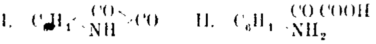
Nitroso-oxindole Amino-oxindole

$$C_6H_4{<}\substack{CO\\N}{>}C\,OH$$

Isatin

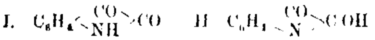
And such a series of reactions formed the coping-stone of the first artificial synthesis of indigotin.

Isatin (I.) is the inner anhydride of *o*-amino-phenylglyoxylic acid (isatinic acid) (II.)



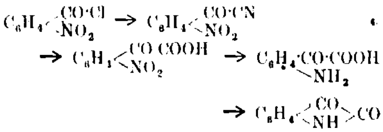
$$\text{I. } C_6H_4{<}\substack{CO\\NH}{>}CO \qquad \text{II. } C_6H_4{<}\substack{CO\,COOH\\NH_2}$$

and such a constitution was predicted for it by Kekulé in 1869 (Ber. 2, 748). Isatin, which possesses acid properties and is capable of forming metallic compounds, may exist as pointed out by Baeyer in two modifications. These are known as pseudo-isatin (lactamisatin) (I.) and isatin (lactimisatin) (II.):



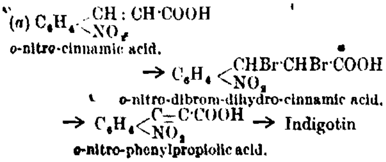
$$\text{I. } C_6H_4{<}\substack{CO\\NH}{>}CO \qquad \text{II. } C_6H_4{<}\substack{CO\\N}{>}C\,OH$$

A synthesis of isatin from *o*-nitro-benzoyl chloride was announced by Claisen and Shadwell in 1879 (Ber. 12, 350), and the reactions involved may be expressed by the following formulæ:—



$$C_6H_4{<}\substack{CO\cdot Cl\\NO_2} \rightarrow C_6H_4{<}\substack{CO\cdot CN\\NO_2} \rightarrow C_6H_4{<}\substack{CO\,COOH\\NO_2} \rightarrow C_6H_4{<}\substack{CO\cdot COOH\\NH_2} \rightarrow C_6H_4{<}\substack{CO\\NH}{>}CO$$

The fact that indole can be prepared from *o*-nitro-cinnamic acid (*l.c.*) and that indole is closely related to indigotin, as indeed was shown by Nencki (Ber. 1875, 8, 727), who prepared indigotin by the action of ozonised air upon an aqueous suspension of indole, led Baeyer to experiment on the synthesis of indigo from this same acid (Ber. 1880, 13, 254). This object he eventually accomplished by the two methods given below:



$$(a)\ C_6H_4{<}\substack{CH:CH\cdot COOH\\NO_2}$$

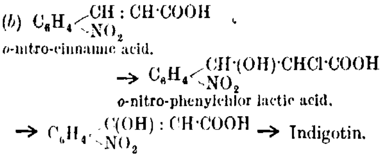
o-nitro-cinnamic acid.

$$\rightarrow C_6H_4{<}\substack{CHBr\cdot CHBr\cdot COOH\\NO_2}$$

o-nitro-dibrom-dihydro-cinnamic acid.

$$\rightarrow C_6H_4{<}\substack{C\equiv C\cdot COOH\\NO_2} \rightarrow \text{Indigotin}$$

o-nitro-phenylpropiolic acid.



$$(b)\ C_6H_4{<}\substack{CH:CH\cdot COOH\\NO_2}$$

o-nitro-cinnamic acid.

$$\rightarrow C_6H_4{<}\substack{CH(OH)\cdot CHCl\cdot COOH\\NO_2}$$

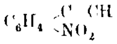
o-nitro-phenylchlor lactic acid.

$$\rightarrow C_6H_4{<}\substack{C(OH):CH\cdot COOH\\NO_2} \rightarrow \text{Indigotin.}$$

o-nitro-phenylacrylic acid.

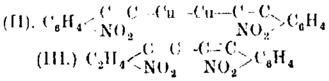
The former method is exceptionally interesting, in that it provided the basis for the first attempt to manufacture indigo on a commercial scale, and though this was hardly successful, the *o*-nitrophenylpropiolic acid obtained by this method was of some service to the dyeing industry, as a means for obtaining indigo prints on calico.

Baeyer, again, in 1882 (Ber. 15, 50) announced a further synthesis employing *o*-nitro-phenylpropiolic acid which was important in connection with the constitution of indigotin. When boiled with water *o*-nitro-phenylpropiolic acid yields *o*-nitro-phenylacetylene



$$C_6H_4{<}\substack{C\equiv CH\\NO_2}$$

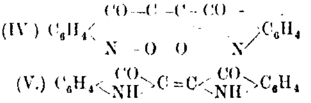
and from the copper compound of this (II.) by oxidation with ferri-cyanide, dinitro-diphenyl-acetylene (III.) is obtained:



$$\text{(II.) } C_6H_4{<}\substack{C\equiv C-Cu-Cu-C\equiv C\\NO_2\qquad\qquad\qquad NO_2}{>}C_6H_4$$

$$\text{(III.) } C_6H_4{<}\substack{C\equiv C-C\equiv C\\NO_2\qquad NO_2}{>}C_6H_4$$

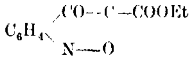
With fuming sulphuric acid this forms diisatogen (IV.), a compound which on reduction gives indigotin (V.):



$$\text{(IV.) } C_6H_4{<}\substack{CO-C-C-CO\\N-O\quad O-N}{>}C_6H_4$$

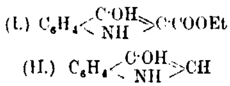
$$\text{(V.) } C_6H_4{<}\substack{CO\\NH}{>}C=C{<}\substack{CO\\NH}{>}C_6H_4$$

o-Nitro-phenylpropiolic acid, on the other hand, by the action of sulphuric acid (Baeyer, Ber. 1881, 17, 1741) is transformed into its isomer isatogenic acid



$$C_6H_4{<}\substack{CO-C-COOEt\\N-O}$$

Reducing agents convert this into ethyl indoxylate (I.) which by heating gives indoxyl (II.):

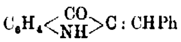


$$\text{(I.) } C_6H_4{<}\substack{C\cdot OH\\NH}{>}C\cdot COOEt$$

$$\text{(II.) } C_6H_4{<}\substack{C\cdot OH\\NH}{>}CH$$

and this latter when oxidised readily passes into indigotin.

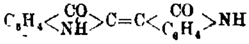
Indoxyl reacts with aldehydes and ketones to form the so-called indogenides. Thus with benzaldehyde the indogenide of benzaldehyde (benzylidene pseudo-indoxyl)



$$C_6H_4{<}\substack{CO\\NH}{>}C:CHPh$$

is produced (Baeyer, Ber. 16, 2188).

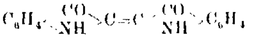
In a similar way indoxyl condenses with isatin to form indirubin



$$C_6H_4{<}\substack{CO\\NH}{>}C=C{<}\substack{CO\\C_6H_4}{>}NH$$

a colouring matter present in natural indigo (*l.c.*), and which is to be regarded as the indogenide of isatin.

Baeyer in 1883 reviewing the facts here enumerated was enabled to deduce the following constitution of indigotin:—



$$C_6H_4\Big<\begin{array}{l}CO\\NH\end{array}\Big>C=C\Big<\begin{array}{l}CO\\NH\end{array}\Big>C_6H_4$$

which is now accepted as correct.[1] The main arguments he employed in support of this formula are as follows:—

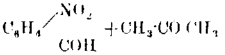
1. Indigotin contains two imido groups.
2. As a result of its formation from diphenyl-acetylene the carbon atoms of indigotin must be arranged in a similar manner to those present in this substance—

$$C_6H_5{\cdot}C{:}C{\cdot}C{:}C{\cdot}C_6H_5$$

3. Indigotin is only formed from compounds in which the carbon atoms adjacent to the benzene ring are united with oxygen.
4. The properties of indigotin point to the fact that it is closely related to indirubin

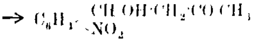
As a result indigotin is to be regarded as the α-indogenide of pseudo isatin, indirubin itself being the β indogenide. Owing, however, to the lack of activity of the α-oxygen atom in isatin, indigotin cannot, like indirubin, be directly prepared from indoxyl and isatin

In 1882 (Ber 15, 2856) Baeyer and Drewsen synthesised indigotin by the action of acetone on *o*-nitro-benzaldehyde in the presence of alkali:



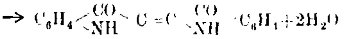
$$C_6H_4\Big<\begin{array}{l}NO_2\\COH\end{array} + CH_3{\cdot}CO{\cdot}CH_3$$

o-nitro-benzaldehyde.



$$\rightarrow C_6H_4\Big<\begin{array}{l}CH{\cdot}OH{\cdot}CH_2{\cdot}CO{\cdot}CH_3\\NO_2\end{array}$$

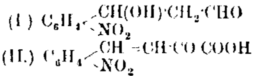
o-nitro-phenyl-lacto-methyl-ketone



$$\rightarrow C_6H_4\Big<\begin{array}{l}CO\\NH\end{array}\Big>C=C\Big<\begin{array}{l}CO\\NH\end{array}\Big>C_6H_4+2H_2O$$

$$+CH_3COOH$$

When the acetone is replaced by acetaldehyde *o*-nitro-phenyl-lactic aldehyde (I.) is obtained, whereas with pyroracemic acid *o*-nitro-cinnamyl-formic acid (II.) is produced:

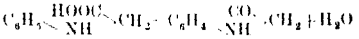


$$\text{(I.)}\ C_6H_4\Big<\begin{array}{l}CH(OH){\cdot}CH_2{\cdot}CHO\\NO_2\end{array}$$

$$\text{(II.)}\ C_6H_4\Big<\begin{array}{l}CH=CH{\cdot}CO{\cdot}COOH\\NO_2\end{array}$$

These compounds under the influence of alkali are transformed into indigotin.

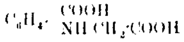
Heumann in 1890 (Ber. 23, 2043) devised the synthesis of indigotin from phenylglycocoll (phenylglycine). This on fusion with alkali is transformed into indoxyl which passes readily by oxidation into indigotin:



$$C_6H_5\Big<\begin{array}{l}HOOC\\NH\end{array}\Big>CH_2 \rightarrow C_6H_4\Big<\begin{array}{l}CO\\NH\end{array}\Big>CH_2+H_2O$$

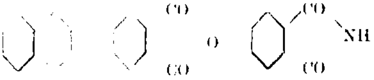
Pseudo-indoxyl.

The yield by this method is extremely small, but this can be improved by employing in the place of phenylglycine, phenylglycine *o*-carboxylic acid (Heumann, *ibid.* 3431):

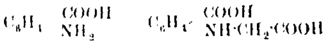


$$C_6H_4\Big<\begin{array}{l}COOH\\NH{\cdot}CH_2{\cdot}COOH\end{array}$$

This important reaction forms the basis of the first economical synthesis of indigo, the large scale manufacturing operations of which were perfected by the Badische Anilin- & Soda-Fabrik in 1897. For the preparation of phenylglycine *o*-carboxylic acid, naphthalene is employed as the starting-point, and the procedure involved will be evident from the following formula:—

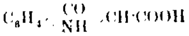


Naphthalene Phthalic anhydride Phthalimide.



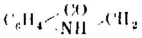
$$C_6H_4\Big<\begin{array}{l}COOH\\NH_2\end{array} \qquad C_6H_4\Big<\begin{array}{l}COOH\\NH{\cdot}CH_2{\cdot}COOH\end{array}$$

Anthranilic acid Phenylglycine *o*-carboxylic acid.



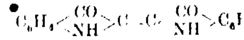
$$C_6H_4\Big<\begin{array}{l}CO\\NH\end{array}\Big>CH{\cdot}COOH$$

Indoxyl carboxylic acid.



$$C_6H_4\Big<\begin{array}{l}CO\\NH\end{array}\Big>CH_2$$

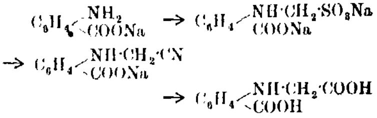
Pseudo-indoxyl.



$$C_6H_4\Big<\begin{array}{l}CO\\NH\end{array}\Big>C=C\Big<\begin{array}{l}CO\\NH\end{array}\Big>C_6H_4$$

Indigotin.

An improved method for the production of phenylglycine *o*-carboxylic acid from anthranilic acid has subsequently been adopted, the reagents employed being formaldehyde, bisulphite, and potassium cyanide:



$$C_6H_4\Big<\begin{array}{l}NH_2\\COONa\end{array} \rightarrow C_6H_4\Big<\begin{array}{l}NH{\cdot}CH_2{\cdot}SO_3Na\\COONa\end{array}$$

$$\rightarrow C_6H_4\Big<\begin{array}{l}NH{\cdot}CH_2{\cdot}CN\\COONa\end{array}$$

$$\rightarrow C_6H_4\Big<\begin{array}{l}NH{\cdot}CH_2{\cdot}COOH\\COOH\end{array}$$

Phenylglycine can be prepared directly from aniline by the same method:

$$C_6H_5NH_2+CH_2O+HCN \rightarrow C_6H_5NH_2CH_2CN$$
$$\rightarrow C_6H_5NH{\cdot}CH_2COOH$$

More recently it has been recognised that the unsatisfactory yield of indigo by the original process of Heumann is due to the presence of water in the alkali fusion. By the replacement of the sodium hydroxide with sodium amide the destructive action of the water is avoided and the fusion can be successfully carried out at a lower temperature. The manufacture of indigo by such a method has been more recently adopted by the firm of Meister Lucius & Brüning at Höchst.

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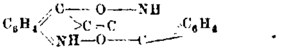
[1] The question, as to how far Baeyer's formula for indigotin is in agreement with the chemical behaviour and physical properties of indigotin, and known facts with regard to the relation between colour and chemical constitution, has been discussed by Madelung (Zeitsch angew. Chem. 1921, 34, 482 *et seq*), who concluded that the facts are more correctly interpreted by the formula

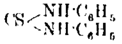


$$C_6H_4\Big<\begin{array}{l}C\text{—}O\text{—}NH\\ \quad >C=C \qquad >C_6H_4\\NH\text{—}O\text{—}C\end{array}$$

The important point in this formula is that the carbonyl and imino-groups are at each end of a five-membered conjugated system, thus $O-C-C=C-NH$. Such an arrangement is to be found in other vat dyes of both the indigoid and anthracene series. Indigotin may thus be regarded as a derivative of the coloured and stable modification of dibenzoylethylene (J. Soc. Chem. Ind. 1921, 730 A).

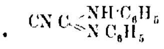
Interesting is also the fact that by treatment with fuming sulphuric acid phenylglycine is converted into indigotin disulphonic acid.

Of other indigo syntheses that of Sandmeyer, at one time employed on the manufacturing scale, is of importance. The starting-point in this method is thio-carbanilide



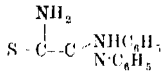
$$CS{<}^{NH\cdot C_6H_5}_{NH\cdot C_6H_5}$$

obtained by the action of carbon disulphide on aniline. This compound by the action of potassium cyanide and lead carbonate forms hydrocyano-carbodiphenylimide



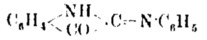
$$CN\,C{<}^{NH\cdot C_6H_5}_{N\,C_6H_5}$$

which on treatment with ammonium sulphide gives the thio-amide



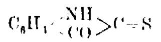
$$S{=}\overset{NH_2}{\overset{|}{C}}{-}C{<}^{NHC_6H_5}_{N\cdot C_6H_5}$$

The latter by heating with sulphuric acid is converted into isatin anilide



$$C_6H_4{<}^{NH}_{CO}{>}C{=}N\cdot C_6H_5$$

and from this by reduction with sulphuretted hydrogen in acid solution thio-isatin is obtained:



$$C_6H_4{<}^{NH}_{CO}{>}C{=}S$$

By the action of dilute alkalis thio-isatin readily passes into indigotin. A. G. P.

INDIGO, ARTIFICIAL, AND INDIGOID DYESTUFFS. The elucidation of the constitution of indigo, the result of the brilliant and indefatigable researches of A. von Baeyer (*v. supra*), has led to consequences of extraordinary importance. The methods discovered for the synthetical production of indigo offered at first little or no prospect of the artificial production of this most important dyestuff at prices which could compete with the natural product. But the patient and unceasing work carried on for that purpose in the laboratories of the Badische Anilin- & Soda-Fabrik in Ludwigshafen gradually surmounted the existing difficulties. Artificial indigo appeared in the market in the year 1897, and was soon acknowledged to be cheaper, purer, and more easy of application than the natural product. New synthetical manufacturing processes which have since then been introduced, combined with a strong competition between the various manufacturers, led to a steady reduction of prices, so that at present (1911) the synthetical dyestuff may be said to have driven out the natural one everywhere, even in countries in which the indigo plants are grown, such as India, the Dutch colonies, China, Japan, and South America. The history of artificial alizarin has been repeated in all its details in the progress of artificial indigo. But the consequences of this new triumph of synthetical chemistry have gone further, in that they have revolutionised the old-established European industries engaged in the production as well as the application of artificial dyestuffs.

The old, but difficult and uncertain process of vat-dyeing, necessary for the application of indigo, has been carefully studied by the factories which had taken up the production of the synthetical product. Sodium hydrosulphite, long known to be the best means for reducing indigo in the vat, but unstable and difficult to prepare, has been brought into new forms in which it is quite stable and easily applied. Thus vat-dyeing has become an operation almost as easy and simple as any other process of dyeing, and the consumers of artificial colouring matters became anxious to be furnished with products similar to indigo in its mode of application and its fastness, but differing in shade. This wish has been satisfied almost simultaneously with its being felt. A large and constantly increasing number of new vat-dyes of every conceivable shade has been offered to the dyer and calico-printer, who is able to use them jointly or in mixtures with indigo, and thus to produce goods, the shades of which are quite as durable as the fibre itself. Some of the new vat-dyestuffs not only equal, but actually exceed indigo in fastness to light, air, and all the other influences which attack and destroy the colour of dyed fabrics. The introduction of the new synthetical vat-dyestuffs has inaugurated a new epoch of fast dyeing, the full importance of which will only be recognised in time to come.

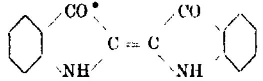
The synthetical manufacture of new colouring matters similar to indigo in their properties was at first the natural consequence of the numerous new syntheses of indigo itself gradually discovered by various chemists, and many of which proved applicable to the production of compounds similar to indigo in their constitution, but differing from it in certain details of composition, and consequently also in their shades. Many of these substances could be made on a large scale, and offered to the consumer at moderate prices. They are now known under the name of 'Indigoids,' and the more important of them will be mentioned further on.

The investigation of indigo and the indigoid dyestuffs led, however, to another result of no small importance. The connection existing between the constitution and the properties of indigo as a dyestuff, so long a mystery, was at last recognised, and the atomic configuration was disclosed which causes a dyestuff to be applicable to vat-dyeing. The natural consequence of this discovery was the possibility of producing, by synthetical methods, a vast number of new vat-dyes, which in their constitution have no longer any similarity to indigo, and the majority of which has been derived from anthraquinone, the mother-substance of alizarin, which has thus assumed a new importance.

The description of these dyestuffs supplementing indigo in its applications, and now already exceeding the indigoids in number is dealt with elsewhere (*see* VAT-DYES, MODERN; INDANTHRENE).

The number of vat-dyes now already in practical use or in the stage of being introduced may be estimated at from 80 to 90, and is constantly increasing. Their discovery is due to the inventive genius of many chemists, amongst whom René Bohn may be considered as the pioneer.

A. **Artificial Indigo.** The constitution of indigo is expressed by the formula :



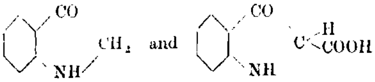
Of the numerous methods which lead to the synthetical production of such a compound very few are applicable to its manufacture, and only the latter will be here mentioned.

The first attempt at a technical synthesis of indigo was made in 1880 by A. von Baeyer in his German patent 11857, which was sold to the Badische Anilin- & Soda-Fabrik and the Höchster Farbwerke jointly. In this *ortho*nitrocinnamic acid is used as a raw material, and transformed into indigo by three different methods. Of these only the one which passes through *ortho*nitrophenylpropiolic acid as an intermediate product found for a short time a limited and almost experimental application as a means of producing indigo on the fibre in calico-printing.

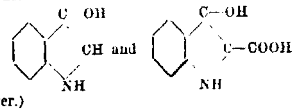
Another method (1882), which consists in adding caustic soda to a solution of *o*-nitrobenzaldehyde in acetone, when the methyl-*o*-nitrocinnamylketone formed as an intermediate product is immediately condensed into indigo, was also, in spite of its simplicity, unable to compete with the natural product.

In 1890 K. Heumann observed that phenylglycine and its *ortho*carboxylic acid are transformed into indoxyl and indoxylcarboxylic acid by being melted with caustic potash ; the orange-coloured melts obtained yield indigo on being oxydised with air in aqueous solution. The patents obtained for these reactions (D. R. P. 54626 and numerous additions ; also D. R. P. 56273 and additions) passed into the hands of the Badische Anilin- & Soda-Fabrik, but were not considered very promising by the majority of chemists. Yet they were destined to assume fundamental importance in the subsequent development of the indigo industry. It is true that a good many other inventions were necessary to raise them to that position.

Indoxyl and indoxylcarboxylic acid have the constitution expressed by the formulæ :



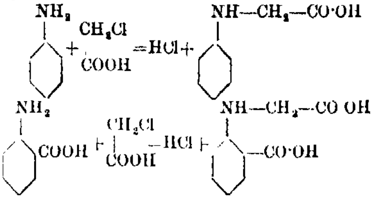
These formulæ represent the so-called 'pseudo'-forms, which are the first products of the reaction. Isolated indoxyl and indoxylcarbonic acid are better represented by the tautomesic formulæ :



(Baeyer.)

On being treated with atmospheric oxygen in alkaline solution the one loses H_2 in the shape of water, the other H_2CO_2 in the shape of carbonic acid (H_2CO_3), and the so-called 'indigo bridge' $>C=C<$ is formed by two such indoxyl complexes being united by double valencies.

Phenylglycine and its *ortho*carboxylic acid are prepared by the action of monochloracetic acid [1] upon aniline and anthranilic acid :



It was observed, that phenylglycine-*o*-carboxylic acid gave better yields of indigo than phenyl-glycine itself, which was, on the other hand, cheaper and more easily accessible. Later on it was found that both these glycines are capable of being transformed into indigo with very good yields if *every trace* of water is excluded from the alkaline melt. The glycine itself is in this respect more susceptible than its carboxyl derivative. Not only the water invariably retained by all the caustic alkalis hinders the reaction, but also the water formed in the reaction itself. One of the means of overcoming this difficulty consists in the addition of finely ground lime or baryta to the melt.

In taking up the manufacture of artificial indigo by Heumann's method in the beginning of the nineties the Badische Anilin- & Soda-Fabrik decided to use phenylglycine-*o*-carboxylic acid as a raw material. This decision was prompted not only by the better yields which were obtained from this product, but even more so by considerations of quite a different nature.

If it had been necessary to produce the anthranilic acid required for the manufacture of indigo by the oxidation of *o*-nitrotoluene and subsequent reduction of the *o*-nitrobenzoic acid thus obtained, all the toluene produced by the distillation of coal-tar would probably not have been sufficient for the purpose. There is, however, another way of producing anthranilic acid which consists in treating phthalimide with alkaline hypochlorites (Hoogewerff's and Van Dorp's process ; D. R. P. 55988, Badische Anilin- & Soda-Fabrik, 1890). Phthalimide is easily obtained by treating phthalic anhydride with ammonia. Phthalic acid, on the other hand, is best prepared by the oxidation of naphthalene.

Thus it became possible, by using phenylglycine-*o*-carboxylic acid as a starting-point for the synthesis of indigo on a large scale, to base this manufacture on the use of naphthalene as its first raw material, a hydrocarbon which is contained in coal-tar in much larger quantities than any other of its constituents.

Even when these conclusions had been arrived at a great deal remained still to be done. It is now known that the Badische Anilin- & Soda-Fabrik had to invest about 1,000,000*l.* in experiments and new plant before artificial indigo could enter the world's market as a rival to the natural product, and that the ultimate success obtained is mainly due to the courage, inventive genius and perseverance of Rudolf Knietsch, who superintended the whole development of this new industry. But it must also be said that the latter found its advent well prepared by the development which chemical industry as a whole had taken towards the end of the nineteenth century. One of the principal advantages produced by that development was the possibility of obtaining chlorine (which is required both for the chloracetic and the anthranilic acid used in the indigo process) and caustic alkalis at extremely low prices owing to the introduction of the electrolytic decomposition of alkaline chlorides.

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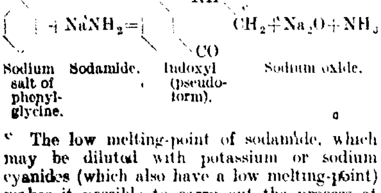
[1] Instead of this acid, prepared in the old manner from acetic acid and chlorine, ethyl monochloracetate may be used, which can be obtained from acetylene by a simple process (D. R. PP. 154657, 171900, 216940, 209268, 210502, and 216716, Imbert and Consortium für electrochemische Industrie, Nürnberg). See also Chemikerzeitung, 1911, p. 1053.

The oxidation of naphthalene into phthalic acid as practised in former times was cumbrous and difficult, and gave very poor yields. A new method was discovered for the purpose which consists in the oxidation of naphthalene polysulphonic acids by means of very strong pyrosulphuric acid. To obtain the latter a new process had to be worked out, now known to the world as the catalytic or contact process (*see* SULPHURIC ACID). A certain quantity of mercuric sulphate must be added in the oxidation of the naphthalene sulphonic acid; its action is purely catalytic and indefinite. The sulphur dioxide formed by the reduction of the pyrosulphuric acid returns continuously into the manufacture of the latter. The oxidation of the naphthalene thus practically takes place by means of atmospheric oxygen, and phthalic anhydride is exceedingly cheap if manufactured on a large scale by this process.

The employment of naphthalene as a raw material rendered it possible for artificial indigo to compete commercially with the natural product. But it was destined to meet itself with a very serious competition which arose from a discovery made by J. Pfleger of the Deutsche Gold- & Silber-Scheide-Anstalt in Frankfurt o/M., who observed that the destructive influence of water in the alkali melt of phenylglycine could be completely eliminated by using, not sodium hydroxide, but sodamide for effecting the transformation of the glycine into indoxyl. Sodium oxide and gaseous ammonia are instantly formed by the water produced in the condensation of the glycine according to the following reaction:—



The low melting-point of sodamide, which may be diluted with potassium or sodium cyanides (which also have a low melting-point) makes it possible to carry out the process at the low temperature of 180°-230° C., which favours the production of almost theoretical yields. Of course the process is also applicable to the transformation of phenylglycine-*o*-carboxylic acid into indigo.

It is true, that sodamide can only be prepared by the action of ammonia upon metallic sodium; its price is therefore a high one; on the other hand, the advantages to be obtained by its use are very great and make it possible for this process to compete with the one adopted by the Badische Anilin- & Soda-Fabrik. It was therefore acquired by the Höchster Farbwerke, who are now producing a considerable share of the world's consumption of indigo.

The enormous increase of the world's production of benzene, caused by the general introduction of by-product coke-ovens, and the very low prices of aniline caused by this overproduction, has also favoured the success of Pfleger's invention.

Other synthetical methods have been devised which lead from aniline to indigo, such as Sandmeyer's and Blank's. But they cannot compete with the methods described, and have therefore never been carried out on more than an experimental scale. For details about these processes, some of which are exceedingly interesting from a theoretical point of view, the existing works on the chemistry of colouring-matters and more especially the patent literature should be consulted. Some of these processes may possibly assume considerable importance as a means of producing indigoid dyestuffs.

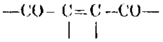
The complete insolubility of indigo in water and aqueous fluids makes it imperative that the dyestuff should be in a state of extremely fine subdivision, and thoroughly moistened before being introduced into the vat. For this reason the dyers used to grind the natural product with a certain proportion of water in the well-known indigo-mills. The unnecessary trouble caused by this preliminary treatment is spared by the form which has been given to the artificial dyestuff, which is generally sold in the shape of a paste containing 20 p.c. of pure indigotin. For export, where the reduction of carriage, and in many countries also the import duties, have to be considered, stronger pastes may be prepared or even the shape of a dry powder is chosen. Much trouble has been taken to reduce the indigo to the greatest possible fineness. All the modern means of powdering and grinding have been utilised, and also the method of precipitating indigo from its solution in sulphuric acid (in which it is contained as a sulphate) by the addition of water has been resorted to.

The world's annual consumption of indigo is estimated at more than 5,000,000 kilograms of the pure dyestuff. In 1900, that is three years after its introduction, the artificial product had secured about one-tenth of this quantity.

At present the shortage in the supply of indigo, which existed from the outbreak of war until the latter part of 1916, has stimulated in a very marked degree the cultivation of the indigo plant. In British India the total area under indigo in 1916–17 was 756,400 acres, being 114 p.c. in excess of the acreage of the preceding year. The corresponding increase in the total yield of indigo was 73 p.c. In 1915 the amount of natural indigo imported into the United Kingdom was 25,157 cwts., whereas in ten months of 1916 the import was 28,245 cwts.; the latter is practically equal to the largest amount of synthetic indigo imported into the United Kingdom during the period 1911–15, the maximum being 28,302 cwts. for the year 1912. This increase in the cultivation of the indigo plant is being accompanied by a systematic and scientific inquiry into the agricultural conditions affecting the growth of the plant, and the formation of indican (G. T. Morgan, Reports of the Progress of Applied Chemistry, 1917, vol. ii. 120).

The valuable properties of indigo as a dyestuff are a function of the peculiar atomic configuration which connects the two phenylene radicles. By the reduction in the vat 2 atoms of hydrogen are taken up by this complex and indigo white is formed, the exact constitution of which is doubtful. But it is now generally acknowledged, that in leuco-indigo hydroxyl groups have replaced the ketonic oxygens of indigo. These hydroxyl groups possess auxochromic characters, and are responsible for the absorption of the indigo white by the fibre. It follows that every other strongly coloured aromatic substance which contains at least two reducible carbonyl groups must be endowed with the properties of a vat-dye. This conclusion has been strictly confirmed by modern investigations and the whole modern development in the production of vat dyes has been built up on it.

B. Indigoids. – The congeners of indigo may be divided into two different classes. One of them contains the true derivatives of indigo, in which one or more of the 8 hydrogen atoms of the two phenylene groups are replaced by other substituents; the other embraces substances which are strictly analogous to indigo in their constitution but different from it in the construction of the complex connecting the two phenylene groups, which in this case as well as in that of indigo may have their hydrogen atoms replaced by other substituents. An enormous variety of new dyestuffs may thus be synthesised, all of which contain the characteristic chromophoric group of indigo:


$$\begin{array}{c}\text{—CO—}\underset{|}{\text{C}}\text{=}\underset{|}{\text{C}}\text{—CO—}\end{array}$$

(*a*) *Substitution products of indigo.*—These may be prepared by treating indigo with suitable reagents or by using suitably substituted ingredients in any of the synthetical methods for the production of indigo.

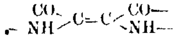
One group of these substitution products has been known for almost a century, and used formerly to be manufactured from natural indigo, viz. the sulphonic acids derived from it, commonly known under the name of *Indigo Carmine.* As these cannot be used as vat-dyes, they need only be mentioned here. They are now invariably prepared from artificial indigo and still used to a moderate extent in wool-dyeing, although they have been largely superseded by other soluble blues. Though derived from one of the fastest dyestuffs known, the indigosulphonic acids are, strangely enough, of an extremely fugitive nature.

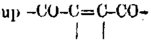
The halogen derivatives of indigo are very numerous. As many as six atoms of chlorine or bromine may be introduced into the molecule of indigo. The properties of the products thus obtained, their shade and fastness, vary strongly not only with the number of halogen atoms introduced, but also with their relative position in the molecule. Of the mono- and di-substituted indigos those which contain their halogen atoms in the *p*-position to the imino groups are very similar to indigo itself; those, on the other hand, in which the *p*-positions to the keto groups are taken up are no longer blue but reddish-violet in shade. The dibromo-indigo corresponding to this condition has been proved by Friedlander to be identical with the *purple of the ancients* (*q.v.*). In spite of the fame which this dyestuff once possessed, modern industry has not thought it sufficiently valuable to be introduced into commerce.

If more than two atoms of halogen be introduced into the molecule of indigo the dyestuffs obtained become more and more brilliant and greenish in shade. The first of these valuable dyestuffs introduced was tetrabromo indigo; it was prepared by the Gesellschaft fur Chemische Industrie in Basle and brought out as '*Ciba*'-*blue* – '*Ciba*' being the distinctive name adopted for all the vat-dyes of this factory. The corresponding tetrachlorinated derivative is '*Brillant indigo* 2B' of the Badische Anilin- & Soda-Fabrik. Penta- and hexabromo-indigo are still more greenish, and are now being manufactured by various firms.

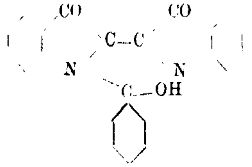
It is, of course, also possible to substitute some of the hydrogen of the indigo molecule by organic radicles. Thus we come to the homologues of indigo, several of which have been prepared. They are all very similar to indigo and offer no special interest. This is also the case with naphthylindigo, the shade of which is a dull green. Its dibromo derivative is much clearer in shade; it has been brought out as '*Ciba-Green G*' by the Basle firm already mentioned.

(*b*) ***Indigoids**, in which the central complex differs from that of indigo.*—In order to understand the nature of these compounds we must reconsider the constitution of indigo. It consists of two phenylene groups, linked together by the complex


$$\begin{array}{ccc}\text{CO}\diagdown & & \diagup\text{CO—}\\ \text{— NH}\diagup & \text{C=C} & \diagdown\text{NH—}\end{array}$$

Now in this complex the group  $\text{–CO–}\underset{|}{\text{C}}\text{=}\underset{|}{\text{C}}\text{–CO–}$ is the indigo chromophore which connects all these dyes into one family and it cannot be touched or altered without destroying the whole character of the compound and its nature as a vat-dye. It follows, that the only changes possible in the central complex of the indigo molecule must be confined to the two imino groups, which may either be altered by their hydrogen being substituted, or by their being shifted into other positions, or by being entirely replaced by other atoms or atomic complexes. All these changes have been accomplished.

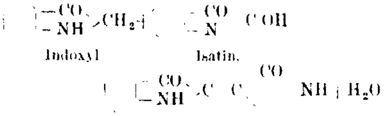
As an interesting example of the first of these alterations two dyestuffs may be mentioned: *Ciba-Yellow G* and *Ciba-Yellow GG.* They are prepared from indigo and tetrabromo-indigo by the substitution of two benzoyl groups for hydrogen in the imino groups. The constitution of Ciba-Yellow G is thus expressed by the formula:



Benzoyl chloride does not act upon indigo under ordinary circumstances, but if a trace of metallic copper be added, its catalytic action causes the substitution of the hydrogen by the benzoyl group. This interesting manufacturing process has been invented by G. Engi.

If the imino groups are to be shifted or to be exchanged for other complexes, this cannot be done by starting from ready-formed indigo. The new dyestuff has to be built up synthetically. According to the synthetical methods adopted we can obtain indigoids of either symmetrical or asymmetrical constitution.

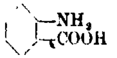
One of the first instances of such a synthesis was the process by which A. von Baeyer prepared Indirubin, the red dyestuff always contained in natural indigo and first observed by Berzelius. This substance is formed if alkaline solutions of indoxyl and isatin are mixed in the cold:



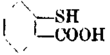
Indirubin

Indirubin is an asymmetrical indigoid in which both the chromophoric complex and the two imino groups are still preserved, but they have changed their relative position in the molecule. Indirubin is of no value as a dyestuff, but its tetrabromo derivative, prepared by G. Engi, is a useful violet and sold under the name *Ciba-Heliotrope*.

If the imino groups are to be exchanged for other divalent complexes, oxygen suggests itself as a suitable substituent. 'Oxygen indigo' has been prepared by Friedlander, but it proved to be a very poor dyestuff. But the same chemist observed in 1905, that sulphur, introduced into the position of the imino groups in indigo, has an excellent effect. A dyestuff of a deep bluish red shade and extraordinary intensity and fastness is formed, which is now known as *Thioindigo red* and manufactured by several firms. It was the first really applicable red indigoid and the process by which Friedländer first prepared it was protected by the German patent 194237 by Kalle & Co. who bought Friedlander's invention. This process is in all its stages strictly analogous to the synthesis of indigo from phenylglycine-*o*-carboxylic acid, but the nitrogen occurring in the latter is everywhere replaced by sulphur. Thus in the first stage anthranilic acid is replaced by thiosalicylic acid

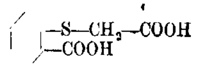


Anthranilic acid.



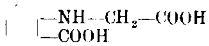
Thiosalicylic acid.

The latter is treated with monochloracetic acid, and thus transformed into



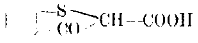
Phenylthioglycine-*o*-carboxylic acid

which is, of course, quite analogous to

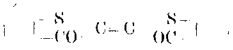


Phenylglycine-*o*-carboxylic acid.

By melting with caustic soda thioindoxylcarboxylic acid



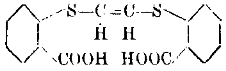
is formed, which, on being oxidised, yields



Thioindigo Red

This process may be simplified by an invention described in the German patent 187586 of the Gesellschaft fur Chemische Industrie in Basle, according to which the phenylthioglycine-*o*-carboxylic acid is simply boiled with nitrobenzene. Condensation and oxydation take place simultaneously and the red dyestuff is deposited in glistening crystals.

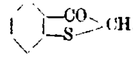
Another extremely simple method for the production of this dyestuff has been invented by E. Munch, and patented by the Badische Anilin- & Soda-Fabrik (French Pat. 385044; German Pat. application B 47813). It consists in treating the salts of thiosalicylic acid with dichloroethylene. This compound, as a rule so reluctant to part with the chlorine it contains, in this case acts most readily, connecting two molecules of the acid, thus forming the whole chain of atoms required:



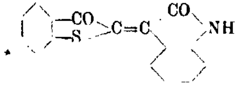
By treating this product with chlorosulphonic acid two molecules of water are eliminated, and the central complex of thioindigo red is formed. It suffices to add water which precipitates the dyestuff in a very pure condition.

Thioindigo red is extremely fast, but unfortunately its shade is not favourable to a very large consumption. An indigoid of a brilliant scarlet shade was required, and this was found in the asymmetrical representative of this group.

Thioindigo Scarlet.—This compound is analogous to indirubin in the same way in which thioindigo red is analogous to indigo, and it is also prepared by the method suggested by this analogy; thioindoxyl



(or, as it is often called, oxythionaphthene) is treated in an alkaline solution with isatin (*see* equation for the formation of indirubin). It has consequently the constitution



and is not only asymmetrical, but also a mixed indigoid, containing both sulphur and the imino group.

Both thioindigo red and scarlet yield many new dyestuffs by the substitution of halogens and other substituents for hydrogen in their phenylene groups. They dye various shades of scarlets, bluish-reds, and reddish-violets, and several of them have come into use as serviceable vat-dyes. O. N. W.

INDIGO COPPER. *Cupric sulphide v.* COPPER.

INDIRUBIN *v.* INDIGO, NATURAL; INDIGO, ARTIFICIAL; INDOXYL COMPOUNDS.

INDIUM. Symbol In. At.wt. 114·8 (Thiel and Mathers) Indium belongs to the aluminium group of the elements, and was discovered in Freiberg zinc blende by Reich and Richter in 1863 by means of spectrum analysis. It also occurs in small quantities in other zinc blendes, in siderites, and in various tungsten and manganese ores (Hartley and Ramage, Chem. Soc. Trans. 1897, 533). The metal can be obtained from the oxide by ignition in a current of hydrogen or by fusion with sodium (Winkler, J. pr. Chem. 1867, 102, 273) It can also be obtained pure electrolytically from the chloride, nitrate, or sulphate (Dennis and Geer, Ber. 1904, 37, 961; Thiel, *ibid.* 175; Mathers, J. Amer. Chem. Soc. 1908, 30, 209).

Indium is a white, readily malleable metal, softer than lead, and is not attacked by air at ordinary temperature. It can be obtained as regular octahedral crystals (Sachs, Zeitsch. Kryst. Min. 1903, 38, 495; Thiel, *l.c.*), having sp gr. 7·277 at 20°, and m.p. 155°. It dissolves slowly in hydrochloric, sulphuric, and nitric acids, and when heated in the blowpipe gives a blue colour and an incrustation of the oxide. Indium forms a series of isomorphous mixtures with lead (Kurnakoff and Pushin, J. Russ. Phys. Chem. Soc. 1906, 38, 1146; Kurnakoff and Schemtschuschny, Zeitsch, anorg. Chem. 1909, 64, 149), and alloys with gold, tin, gallium, and sodium. It also combines with selenium and tellurium, forming black masses with a metallic lustre (Renz, Ber. 1904, 37, 2110). In its compounds, indium appears as mono-, di-, and tri-valent, but only the latter are stable in aqueous solution.

Indium oxide In_2O_3 is a pale yellow powder which, according to Renz (Ber. 1903, 36, 1847), is converted into two other amorphous modifications when strongly heated (Meyer, Zeitsch. anorg. Chem. 1905, 47, 281). At 1000° the oxide is partially converted into chlorine-green shining crystals (Renz, *l.c.* 2751; Thiel, *l.c.* and Ber. 1906, 48, 201). A lower oxide, In_3O_4, also exists.

Indium hydroxide $In(OH)_3$ resembles aluminium hydroxide, is converted into the oxide by heating, dissolves in potash but not in ammonia and readily forms colloidal solutions in the absence of electrolytes.

Indium hydroxide behaves towards bases as a weak acid; when carefully dried at 100°, the *meta* acid In·O·OH is obtained, and the corresponding magnesium indate $(InO)_2O_2Mg,3H_2O$ is formed by boiling a solution of indium chloride with magnesium chloride (Renz, Ber. 1901, 34, 2763 and *l.c.*).

Halogen salts. Indium forms three *chlorides*, InCl, $InCl_2$, $InCl_3$; the last forms a crystalline compound with pyridine

$$InCl_3 \cdot 3C_5H_5N$$

m.p. 253° (Dennis and Geer, *l.c.*; Chabrié and Rengade, Compt. rend. 1901, 132, 472). Three corresponding *bromides* (Thiel, Ber. 1904, 37, 175), and *iodides*, the *trifluorides*, $InF_3,3H_2O$ and $InF_3,9H_2O$ (Thiel, *l.c.*; Chabrié and Bouchonnet, Compt. rend. 1905, 140, 90), an *oxychloride* InOCl, an *iodate*, and a *perchlorate* (Schluederberg, J. Amer. Chem. Soc. 1908, 30, 211) are known.

Indium trisulphide In_2S_3 is a scarlet powder with metallic lustre which, when heated in hydrogen, forms the monosulphide In_2S, which is a brown powder. Both sulphides can be obtained in a crystalline form (Thiel, *l.c.*).

Basic indium sulphite $In_2(SO_3)_3In_2O_3,8H_2O$ is a crystalline powder which is obtained when an indium salt is boiled with acid sodium sulphite.

Indium also forms *sulphates*, *nitrates*, the *molybdate* $In_2(MoO_4)_3,2H_2O$, the *platino-cyanide* $In_2[Pt(CN)_4]_3$ (Renz, *l.c.*), a *selenate* (Schluederberg, *l.c.*), *uranate*, *tungstate*, and *silico-tungstates* (Wyrouboff, Bull. Soc. Franç. Min. 1907, 30, 277).

Indium ammonium alum

$$In_2(SO_4)_3(NH_4)_2SO_4,24H_2O$$

(also with $8H_2O$) forms well-defined regular octahedra. Similar alums are formed with the sulphates of rubidium and cæsium, but the analogous salts with potassium and sodium are not pure alums (Chabrié and Rengade, Compt. rend. 1900, 131, 1300; 1901, 132, 472). For its spark spectrum, *v.* Schulemann, Zeitsch. wiss. Photochem. 1911, 10, 263.

INDOFORM. Trade name for a mixture of salicylic acid, acetyl salicylic acid, moistened with formaldehyde solution, dried, and perfumed with methyl salicylate (*v.* SYNTHETIC DRUGS).

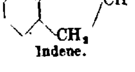
INDOINS (*Safranine azo-colouring matters*). The name Indoin blue R is given to the basic tannin colouring matter which is formed by combining the diazonium salt prepared from safranine and nitrous acid with β-naphthol. The compound is of some technical importance and dyes both unmordanted and tannined cotton fast indigo shades of blue.

The name indoin was also given by Baeyer (Ber. 1881, 14, 1741) to a blue compound resembling indigo, having the composition $C_{32}H_{20}O_5N_4$, prepared by the action of reducing agents, for example ferrous sulphate, on phenylpropiolic acid dissolved in sulphuric acid.

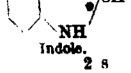
J. F. T.

INDOLES. To this class belong a series of compounds, many members of which are of considerable importance from the bio-chemical standpoint.

They are derived from indole C_8H_7N, a compound which is related to indene in the manner shown by the following formulæ:—



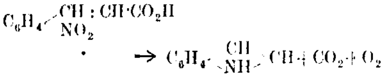
Indene.



Indole.

The indole derivatives which occur in the organism are more or less closely related to tryptophan (*q.v.*), a substance which, according to the latest investigation is an indole-amino-propionic acid.

Indole was first obtained by Baeyer by distilling with zinc dust, either oxindole $C_6H_4\left<\begin{array}{l}CH_2\\NH\end{array}\right>CO$, or the product obtained by reducing indigo with tin and hydrochloric acid. It is also formed when *o*-nitrocinnamic acid is distilled with caustic potash and iron filings (Baeyer and Emmerling, Ber. 1869, 2, 680):



$$C_6H_4\left<\begin{array}{l}CH:CH\cdot CO_2H\\NO_2\end{array}\right. \rightarrow C_6H_4\left<\begin{array}{l}CH\\NH\end{array}\right>CH+CO_2+O_2$$

It can also be produced by passing the vapour of ethyl aniline and other alkyl anilines through a red-hot tube (Baeyer and Caro, Ber. 1877, 10, 692, 1262), but the best method of preparation is by the action of dichlorether

$$CH_2Cl\cdot CHCl\cdot OC_2H_5$$

on aniline. A mixture of 50 grams of aniline with an equal bulk of water is heated, and to the boiling liquid 25 grams of dichlorether are gradually added. The boiling is continued for an hour, after which the water and excess of aniline are distilled off and the residue is heated for about 4 hours at 210° 230°. On distilling the product with steam, indole passes over and may be purified by conversion into the picrate. In this reaction, ethylidene di-aniline is first formed which, on heating to a higher temperature, breaks down into indole and aniline, thus:

$$C_6H_5N:CH\cdot CH_2\cdot NHC_6H_5\rightarrow C_8H_7N+C_6H_5NH_2$$

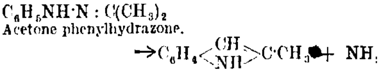
Indole forms colourless, lustrous laminæ, melts at 52° and boils with partial decomposition at 253°–254°. It is readily volatile in steam and is easily soluble in boiling water and in alcohol, ether, and benzene. When nitrous acid is added to an aqueous solution of indole, containing nitric acid, nitrosoindole nitrate is precipitated in the form of small red needles. An aqueous solution, or the vapour of indole, colours a pine chip moistened with hydrochloric acid and alcohol cherry-red, the colour afterwards changing to reddish-brown. Indole suspended in water and oxidised with ozone yields traces of indigo (Nencki, Ber. 1875, 8, 727). Indole is a weak base and forms, with concentrated hydrochloric acid, a sparingly soluble salt which is dissociated by boiling with water; the picrate is precipitated as dark red needles when a solution of indole in light petroleum is treated with picric acid.

Acetylindole $C_8H_6N(C_2H_3O)$, which is formed by the action of acetic anhydride, melts at 182°–183°. Indole accompanies scatole as a product of the putrefaction of albumen.

Derivatives of indole.—The homologues of indole are most readily obtained by heating the phenylhydrazones of ketones of the formula

$$R'\cdot CO\cdot CH_3 \text{ or } R'\cdot CO\cdot CH_2R'$$

or the phenyl hydrazones of the aldehydes of the formula $R'\cdot CH_2\cdot CHO$, with zinc chloride at 180°. The zinc chloride abstracts the elements of ammonia thus:



$$C_6H_5NH\cdot N:C(CH_3)_2$$

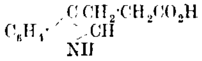
Acetone phenylhydrazone.

$$\rightarrow C_6H_4\left<\begin{array}{l}CH\\NH\end{array}\right>C\cdot CH_3+NH_3$$

β-Methylindole.

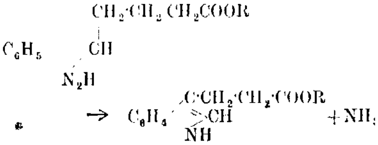
but the reaction is difficult to express by means of structural formulæ. Indole itself cannot be prepared by this reaction.

Indole-3-propionic acid (scatole-acetic acid)



$$C_6H_4\left<\begin{array}{l}C\cdot CH_2\cdot CH_2CO_2H\\ \quad\quad >CH\\NH\end{array}\right.$$

This substance was isolated by Nencki (Monatsh 1889, 10, 506) from the products of the putrefaction of albumen. It has been synthesised by Ellinger (Ber. 1905, 38, 2884) by the action of alcoholic sulphuric acid on the phenylhydrazone of γ aldehydo*iso*butyric ester:

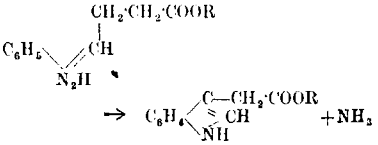


$$\begin{array}{lll} & & CH_2\cdot CH_2\,CH_2COOR\\ & & \quad|\\ C_6H_5 & & CH\\ & N_2H & \end{array}$$

$$\rightarrow C_6H_4\left<\begin{array}{l}C\cdot CH_2\cdot CH_2\cdot COOR\\ \quad\quad >CH\\NH\end{array}\right. +NH_3$$

The acid crystallises from water as prisms which melt at 134°.

Indole-3-acetic acid (scatole carboxylic acid) $C_6H_4\left<\begin{array}{l}C\cdot CH_2\cdot COOH\\ \quad >CH\\NH\end{array}\right.$. This substance was isolated by E. and H. Salkowski (Ber. 1880, 13, 2217) from the products of the putrefaction of albumen. It has been prepared by Ellinger (Ber. 1904, 37, 1803) by the action of alcoholic sulphuric acid on the phenyl hydrazone of methyl aldehydopropionate



$$\begin{array}{lll} & & CH_2\cdot CH_2\cdot COOR\\ & & \quad|\\ C_6H_5 & & CH\\ & N_2H & \end{array}$$

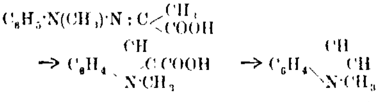
$$\rightarrow C_6H_4\left<\begin{array}{l}C\text{—}CH_2\cdot COOR\\ \quad\quad >CH\\NH\end{array}\right. +NH_3$$

The acid forms small leaflets from a benzene solution which melt at 165° and at the same time eliminate carbon dioxide, yielding scatole.

Scatole (3-methylindole) $C_6H_4\left<\begin{array}{l}C\cdot CH_3\\ \quad >CH\\NH\end{array}\right.$. This substance occurs as a product of the putrefaction of albumen and is also formed by the fusion of protein substances with potash. It was first discovered in human fæces, of which it forms the chief volatile constituent (Brieger, Ber. 1879, 12, 1986); it also occurs in the wood of the *Celtis cinnamomea* (Linol.), Java (Dunstan, Chem Soc. Proc. 46, 211). It is formed with indole when the product obtained by reducing indigo by means of stannous chloride is distilled with zinc dust (Baeyer, Ber. 1880, 13, 2339), and can be prepared by heating the phenylhydrazone of propionic aldehyde $CH_3\cdot CH_2CH:N_2H\cdot C_6H_5$, with an equal weight of zinc chloride and distilling the product with steam, or by heating tetrahydroquinoline at 180° in presence of nickel.

Scatole forms lustrous laminæ, melts at 95° and boils at 265°–266° (corr.) under 755 mm. pressure. It usually has a strong fæcal smell, but when pure is stated to be without odour. It dissolves in concentrated hydrochloric acid, forming a violet solution.

1-Methylindole $C_6H_4\langle\begin{smallmatrix}CH\\N\cdot CH_3\end{smallmatrix}\rangle CH$. When the methylphenylhydrazone of pyruvic acid is treated with hydrochloric acid it parts with the elements of ammonia, yielding 1-methylindolecarboxylic acid



$$C_6H_5\cdot N(CH_3)\cdot N : C\langle\begin{smallmatrix}CH_3\\COOH\end{smallmatrix} \rightarrow C_6H_4\langle\begin{smallmatrix}CH\\N\cdot CH_3\end{smallmatrix}\rangle C\cdot COOH \rightarrow C_6H_4\langle\begin{smallmatrix}CH\\N\cdot CH_3\end{smallmatrix}\rangle CH$$

On heating this compound to 205° it parts with carbon dioxide, forming 1-methylindole (E. Fischer and Hess, Ber. 1884, 17, 562). According to Carrasco and Padoa (Gazz. chim. ital. 1907, 37, II, 49), this substance is also formed when dimethyl-*o*-toluidine is dropped into a tube filled with reduced nickel heated to 300°–330°.

1-methylindole is a yellow oil which boils at 240°–241° (corr.) under 720 mm. pressure. It has sp. gr. 1·0707 at 0° and does not solidify at −20°. It colours a pine chip moistened with hydrochloric acid reddish-violet.

2-Methylindole $C_6H_4\langle\begin{smallmatrix}CH\\NH\end{smallmatrix}\rangle C\cdot CH_3$. This compound is formed from *o*-nitrophenylacetone by reduction with zinc-dust and ammonia, when the *o*-aminophenylacetone, which is first formed in the reaction, eliminates water and passes into 2-methyl indole (Baeyer and Jackson, Ber. 13, 187). It can also be formed by heating acetone phenylhydrazone with five times its weight of zinc chloride for half an hour on the water bath and then for a few minutes at 180° (E. Fischer, Annalen, 236, 126). 2-Methylindole forms needles or laminæ, melts at 59°–60° and boils at 272° (corr.) under 750 mm. pressure. It has a smell resembling that of indole, is sparingly soluble in boiling water, but readily dissolves in alcohol and in ether. It colours a pine chip moistened with hydrochloric acid red.

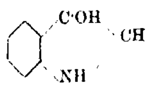
J. F. T.

INDONES *v.* Indene.

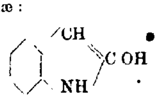
INDOPHENOLS *v.* Indamines and Indophenols.

INDOPYRIN *v.* Synthetic drugs

INDOXYL COMPOUNDS. When the hydrogen atom attached to one or other of the two carbon atoms present in the five-membered ring of indole is replaced by hydroxyl, two isomeric compounds may be formed which are represented by the two formulæ :

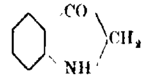


Indoxyl (enol form), stable.

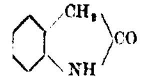


pseudo-Oxindole (enol form), labile.

The presence of the complex CH : C(OH) in these compounds causes them to react in two forms, which may be represented by the further formulæ :



pseudo-Indoxyl (keto form), labile.



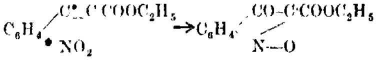
Oxindole (keto form), stable.

The two modifications are, in these cases, tautomeric, that is to say, only one form can be isolated (stable form), but this variety can, under certain conditions, yield derivatives of the other modification (labile form).

As shown by the above expressions, the enol (or hydroxy) form of indoxyl is the stable variety of this substance, whereas the stable form of oxindole (*q.v.*) is represented by the keto structure.

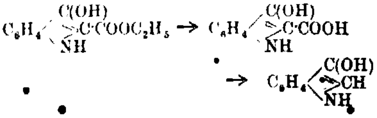
Indoxyl $C_6H_4\langle\begin{smallmatrix}C\cdot OH\\NH\end{smallmatrix}\rangle CH$. The isolation of indoxyl was first effected in the following way. It had been noticed in the 18th century that under certain conditions human urine deposited a blue colouring matter, and the first recorded observation of this fact is ascribed by Thudichum (A Treatise on the Pathology of Urine, London, 1877) to Janus Planchus, in the year 1767. Schunck, in 1857, suggested that the chromogen of this blue colouring matter, which had previously been identified as indigo by Heller and Kletzinski, was the same as indican which he had isolated from woad. This was, however, disproved by Baumann (Pflüger's Archiv 13, 291), who, with Brieger (Zeitsch. physikal. Chem. 1879, III, 258), isolated the chromogen from urine and showed it to be indoxyl sulphuric acid.

Subsequently, Baumann and Tiemann (Ber. 1880, 13, 415) showed that, like phenol sulphuric acid, indoxyl sulphuric acid is decomposed by acids into sulphuric acid and a phenolic substance—indoxyl—and that this compound is quantitatively converted into indigo on oxidation. Subsequently, the synthesis of indoxyl was effected by Baeyer (Ber. 1881, 14, 1741) by the following series of reactions. Ethyl *o*-nitrophenyl propiolate is first converted by shaking with concentrated sulphuric acid into ethyl isatogenate (molecular rearrangement) :



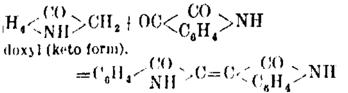
$$C_6H_4\langle\begin{smallmatrix}C\equiv C\cdot COOC_2H_5\\NO_2\end{smallmatrix} \rightarrow C_6H_4\langle\begin{smallmatrix}CO-C\cdot COOC_2H_5\\N-O\end{smallmatrix}$$

This substance on reduction yields ethyl indoxylate, which is then hydrolysed by caustic soda to the sodium salt of indoxylic acid, and the free acid from this, when boiled with water, is transformed into carbon dioxide and indoxyl.



$$C_6H_4\langle\begin{smallmatrix}C(OH)\\NH\end{smallmatrix}\rangle C\cdot COOC_2H_5 \rightarrow C_6H_4\langle\begin{smallmatrix}C(OH)\\NH\end{smallmatrix}\rangle C\cdot COOH \rightarrow C_6H_4\langle\begin{smallmatrix}C(OH)\\NH\end{smallmatrix}\rangle CH$$

Indoxyl when pure forms pale yellow crystals which melt at 85°, but crystallisation cannot be effected in the presence of even slight traces of impurities. It dissolves in water, forming a fluorescent solution and is readily soluble in most organic solvents. It is very unstable and adily oxidises when exposed to the air; the ridation to indigo takes place rapidly in alkane solution. It is volatile with steam and hen treated with isatin in the presence of otassium carbonate is converted into indirubin, reaction which may be represented by the llowing equation :

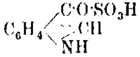


$$\mathrm{H_4}<\substack{\mathrm{CO}\\ \mathrm{NH}}>\mathrm{CH_2} + \mathrm{OC}<\substack{\mathrm{CO}\\ \mathrm{C_6H_4}}>\mathrm{NH}$$

doxyl (keto form).

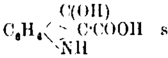
$$=\mathrm{C_6H_4}<\substack{\mathrm{CO}\\ \mathrm{NH}}>\mathrm{C{=}C}<\substack{\mathrm{CO}\\ \mathrm{C_6H_4}}>\mathrm{NH}$$

Indirubin



Indoxyl sulphuric acid $\mathrm{C_6H_4}\begin{array}{l}\diagup\mathrm{C\cdot O\cdot SO_3H}\\ \quad\gg\mathrm{CH}\\ \diagdown\mathrm{NH}\end{array}$

his substance occurs as the potassium salt *dicanuria*) in human urine as well as in the ine of certain carnivora. It occurs to a conlerable extent in the urine of a dog which has en fed on indole. It can be prepared synetically from the potassium compound of doxyl by treatment with potassium pyrolphate (Baeyer, Ber. 1881, 14, 1744) and also fusing phenylglycine-*o*-carboxylic acid and ating the melt with potassium pyrosulphate aumann and Thesen, Zeitsch. physiol. Chem 96, 23, 23). The free acid is unstable, but the tassium salt forms characteristic glistening flets from alcohol in which it is sparingly luble.

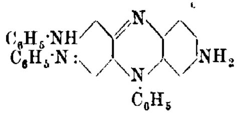


Indoxylic acid $\mathrm{C_6H_4}\begin{array}{l}\diagup\mathrm{C(OH)}\\ \quad\gg\mathrm{C\cdot COOH}\\ \diagdown\mathrm{NH}\end{array}$ separates hen a solution of its sodium salt is acidified a white crystalline precipitate which melts 122°–123° with vigorous evolution of carbon oxide. J. F. T.

INDULINES. A very numerous class of ue colouring matters belonging or closely lated to the safranine group of colours. hey are prepared by heating an aminoazo-compound with an amine in the presence of the loride of the latter. As might be expected, ich a process allows of an almost infinite series variations, and a great number of the colours ave at various times been made and used.

By far the most important is also the earliest nown; the details of its preparation, described elow, are practically those of all the others.

250 kilos. of aniline are mixed with 24 kilos. f hydrochloric acid (35 p.c.) and a solution of 4·4 kilos. of sodium nitrite is run in. The iixture is allowed to remain for some time and hen heated with steam to 40°–50° in order to omplete the transformation of the diazbaminoenzene into aminoazobenzene. The product is then transferred to a cast-iron still capable of olding twice the volume of the melt made in it nd provided with an agitator, swan neck, harging hold, thermometer tube, and discharge alve. 60 kilos. of aniline salt (aniline hydrohloride) are added and the mixture is heated radually so that at the end of about 4 hours the emperature of the melt has reached 175°–180° Schultz, Chemie des Steinkohlentheers, 3rd dit. 1901, ii. 343). The mass is now rendered lkaline with aqueous sodium hydroxide, the xcess of aniline distilled off with a current of team and the residue ground, washed, and lried. A medium shade, as produced by this method, is known as **Induline 3 B spirit soluble**; the formula of its chief constituent is



Red shade indulines (*e.g.* **Fast blue R spirit soluble**) are formed by heating the mixture for a short time only and at a lower temperature (160°–170°). The bluer shades *e.g.* **Fast blue spirit soluble; Induline 6 B spirit soluble**) are obtained by more prolonged heating.

Much of the induline base prepared in this way is sulphonated, but some is dissolved in acetin, lævulic acid, or ethyltartaric acid, forming blue to violet-blue liquors which are used for printing (**Printing blue, Acetin blue, Lævulin blue**, &c.). When spirit-soluble induline is sulphonated it is converted into a sulphonic acid, the sodium salt of which is soluble in water. In this form, various brands of water-soluble indulines are placed on the market under the names of **Induline** (various marks), and **Fast blues.** Another series of blue to blue-grey or black dyes, called **Nigrosines**, is produced by heating aniline and aniline hydrochloride with nitrobenzene or nitrophenol or both in the presence of iron borings. Typical processes are (*a*) *With nitrobenzene*: 175 parts of aniline, 175 parts of nitrobenzene, 200 parts of hydrochloric acid, and 16 parts of iron borings are heated for 8 hours at 160°–200° until a test portion can be drawn out into a thread. The melt is then run out into an iron tray and ground. (*b*) *With nitrophenol*: 100 parts of aniline hydrochloride, 50 parts of aniline, 50 parts of nitrophenol, and a little iron are heated for 10 hours to 180°. (*c*) *With nitrobenzene and nitrophenol*: 183 parts of aniline hydrochloride, 183 parts of nitrobenzene, 137 parts of aniline, 12 parts of crude nitrophenol, and 3 parts of iron borings are slowly heated for a day, the final temperature being about 215°. Towards the end the melt must be constantly tested and run out immediately it begins to thicken, otherwise it will set in the pan and then must be chipped out when cold. The spirit-soluble nigrosines produced, as described above, are sulphonated as in the case of the indulines, the products being known as **Nigrosine soluble.** J. C. C.

INDURITE *v.* EXPLOSIVES.

INFUSORIAL EARTH *v.* KIESELGUHR.

INGRAIN BROWN, -ORANGE, -RED, *v.* AZO- COLOURING MATTERS.

INGRAIN COLOURS *v.* PRIMULINE AND ITS DERIVATIVES.

INK. A coloured fluid used in writing, printing, &c. (Gr. *engkauston—engkaio*, to burn in; Lat. *encaustum*, the purple-red ink used only in the signature of the emperors; It. *inchiostro*; Fr. *encre*; Dutch, *inkt*.)

The writing ink of the ancients consisted of lampblack suspended in a solution of gum or glue. Such inks are still used to a limited extent in the East. Iron-gall inks have been known since the eleventh century. Such ink, as commonly prepared, is a ferroso-ferric gallate suspended in a solution of gum in water, obtained by adding a decoction of substances containing tannin (usually nut-galls) to a solution of ferrous sulphate.

Galls contain gallotannic and gallic acids, which, with ferric salts, form a black precipitate; with ferrous salts the precipitate is white, but becomes black when oxidised by exposure to air. A proportion of gum is added for the purpose of suspending the precipitate equally throughout the solution and of preventing its deposit.

Although other materials may be used, it has been found that the best properties of writing ink—viz. fluidity, penetration, and permanence—are obtained by the use of the ingredients above-named. Such inks fall into two main classes.

Tannin-iron inks are manufactured from the above materials without additions and without previous treatment of the materials. The following typical recipes are taken from the sources named:—

No. 1 (Cooley's Cyclopædia).—Aleppo galls, well bruised, 4 oz.; clean soft water 1 quart; macerate in a clean corked bottle for 10 days or a fortnight, or even longer, with frequent agitation; then add 1¼ oz. of gum arabic dissolved in a wineglassful of water and ½ oz. lump sugar; mix well, and afterwards further add of ferrous sulphate (green copperas), crushed small, 1½ oz.; agitate occasionally for 2 or 3 days, when the ink may be decanted for use, but is better if the whole is left to digest together for 2 or 3 weeks. *Product*: 1 quart of excellent ink, writing pale at first, but soon turning intensely black.

No. 2 (Ure).—12 lbs. of nut-galls, 5 lbs. ferrous sulphate, 5 lbs. Senegal gum, 12 gallons of water. The bruised nut-galls are to be put into a cylindrical copper of a depth equal to the diameter, and boiled during 3 hours with three-fourths of the above quantity of water, taking care to add fresh water to replace what is lost by evaporation. The decoction is to be emptied into a tub, allowed to settle, and, the clear liquid being drawn off, the lees are to be drained. The gum is to be dissolved in a small quantity of hot water, and the mucilage thus formed, being filtered, is added to the clear decoction. The ferrous sulphate must likewise be separately dissolved and well mixed with the above. The colour darkens by degrees in consequence of the peroxidation of the iron on exposing the ink to the action of the air. *Product*: 12 gallons.

No. 3 (Lehner, Ink Manufacture, p. 28).
Ingredients—

Galls . . .	1200	parts by weight.
Ferrous sulphate .	800	,, ,,
Gum arabic . .	800	,, ,,
Water . . .	24,000	,, ,,
Creosote . .	3	,, ,,

Cover the galls with part of the water and dissolve the green vitriol, gum, and creosote separately in the rest of the water. Pour the solution on to the galls, cover up the vessel, and allow to stand for 3 weeks, stirring every day. The ink will then have reached its full blackness and can be bottled for use.

In other processes the galls are repeatedly extracted with boiling water and the extracts united and then mixed with the other constituents; or the tannin is extracted from the bruised galls with ether and the dry product dissolved in water for ink-manufacture. The quality of the product seems to be equally good whatever method is used, provided the ratio between the weights of galls and of ferrous sulphate taken is always about 3 : 2. The addition of an antiseptic substance such as carbolic acid is to be recommended, as the ink is thus preserved indefinitely from the attacks of mould.

Gallic acid inks are also made from galls, ferrous sulphate, gum, and water, with the difference that the galls are first allowed to ferment, whereby the quercotannic acid is converted into gallic acid. The following is a typical recipe:—

Gall nuts	50	parts.
Ferrous sulphate . .	10	,,
Gum	10	,,
Water	2000	,,
Carbolic acid . .	2	,,

The crushed galls are soaked in the water and allowed to ferment. The mass may be inoculated with mould from a mouldy piece of bread or leather. After 8 to 10 days, boiling water is poured on to kill the ferment and the liquid drawn off and used to dissolve the other ingredients.

These inks have a fine blue-black colour and are not so susceptible to change as the tannin inks, but they have fallen into disfavour because they must be partially oxidised before use and thus take a considerable time to manufacture, and even then give a very pale impression on paper. Most of the inks now used contain a '*provisional colouring matter*,' such as indigo and aniline blue, the function of which is to render the ink easily visible at the time of writing and until such time (7–10 days) as it shall be completely oxidised to black ferric gallate.

Logwood tannin inks have been in use since the eighteenth century, and are made by substituting logwood chips or logwood extract for part of the galls in a tannin-ink recipe, *e.g.*:

Galls	30	parts.
Ferrous sulphate . .	36	,,
Logwood extract . .	9	,,
Gum	36	,,
Water	300	,,
Vinegar	60	,,

The method of preparation is similar to that already described.

Logwood gallic acid inks are similarly made but with preliminary fermentation of the galls. These inks have a deep blue-black colour and attack steel nibs less than pure tannin inks.

Alizarin inks are those inks which contain a provisional colouring matter other than logwood. They contain a sufficient proportion of acid (sulphuric or acetic) to keep the iron gallate or tannate in solution, and therefore may be prepared with much less gum than those previously described.

Of the colouring matters used the most important is indigo-carmine, which is prepared by dissolving dry indigo in fuming sulphuric acid, and after 24 hours neutralising with potassium carbonate. The free acid in the indigo solution may also be used to dissolve metallic iron, thus dispensing with the use of green vitriol.

The following recipe is stated to produce an excellent ink :—

Galls	40	parts.
Iron solution	15	„
Indigo-carmine	5	„
Gum	10	„
Pyroligneous acid	10	„
Water	100	„

The galls are powdered and soaked in the water and half the acid for a week. The iron solution is prepared from scrap iron and crude pyroligneous acid left together for a week. These solutions are then mixed and the other ingredients added.

At the present time, many other tannin-containing substances, besides galls, are used in the manufacture of inks. It has been shown that *sumach*, *valonia*, and *logwood* produce an ink which is indistinguishable from gall-inks (Hinrichsen and Kedesdy, J. Soc. Chem. Ind 1909, 831), and good inks may be produced from tanner's barks (elm, oak, pine, poplar, willow, &c.), cutch, gum kino, fustic, elder-berries, the unripe fruit of the chestnut, walnut, &c.

In many cases other and cheaper synthetic dyes are substituted for the indigo-carmine, but this is not necessarily detrimental to the quality of the ink.

Mitchell (Analyst, 1908, 33, 81) has analysed a large number of English writing inks and finds that, although the composition of any one manufacturer's ink remains fairly constant over long periods, there are marked differences between the inks of different manufacturers. The total solid matter ranges from 1·89 to 7·94 p.c., the ash from 0·42 to 2·52 p.c., and the iron from 0·18 to 1·09 p.c.

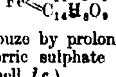
The age of handwriting can be estimated up to the seventh or eighth day, when oxidation is complete, but after that no distinction can be made until the provisional colour begins to fade, usually after about a year.

The bleaching effect of air and light on ordinary writing ink is probably due to the action of hydrogen peroxide, and the permanence of writing by most modern writing inks may be tested by this reagent. Carbon inks are but little affected by hydrogen peroxide or other bleaching agents, and hence afford the most permanent writing (*cf.* Mitchell, Analyst, 1920, 247).

It is probable that in oxidised ink the iron exists as the tannate

$$((C_{14}H_9O_9)_3Fe{\cdot}Fe(C_{14}H_9O_9)_3$$

described by Wittstein (J. 1848, 28, 231) and by Schiff (Annalen, 1875, 175, 176). (*See* also Ozorowitz, Chem. Zentr. 1908, 2, 1024.) As the oxidation proceeds the successive precipitates contain more iron, and eventually approximate in composition to



$$\begin{matrix} Fe \begin{cases} C_{14}H_8O_9 \\ C_{14}H_9O_9 \end{cases} \\ | \\ Fe \begin{cases} C_{14}H_8O_9 \\ C_{14}H_8O_9 \end{cases} \end{matrix}$$

obtained by Pelouze by prolonged exposure of a solution of ferric sulphate and gallotannic acid to air (Mitchell, *l.c.*).

Runge prepared a writing fluid, under the name of 'chrome ink,' which was cheap, intensely coloured, non-corrosive to steel pens, and extremely permanent on paper. The manner of preparing chrome ink is as follows: 1 part of potassium chromate (not dichromate) is added to 1000 parts of a saturated solution of logwood made by boiling 22 lbs. of logwood in a sufficient quantity of water to give 14 gallons of decoction. The potassium chromate is introduced gradually when the solution is cold, the mixture being constantly stirred during the addition. Gum is injurious to the mixture. It may be prepared more simply by dissolving 2000 parts of logwood extract in a solution of 10 parts of pure potassium chromate in 100,000 parts of water.

Prussian regulations for official tests of ink. According to the Prussian regulations of May 22, 1912, inks are classified into (1) 'documentary,' and (2) 'writing inks,' the latter being subdivided into (*a*) iron-gall inks, and (*b*) logwood and dyestuff inks. (1) A 'documentary ink' is defined as an iron-gall ink which gives dark writing after 8 days' exposure to light and air. It must contain at least 27 grams of anhydrous gallotannic and gallic acids, and 4 grams of iron (calculated upon the metal) per litre. On the other hand, the amount of iron must not exceed 6 grams, so that the ratio of gallotannic and gallic acid to iron must lie within the limits 4·5 : 1 and 6·75 : 1. The ink must not alter for at least 14 days in the ink-pot, and must flow readily from the pen. The writing done with it must not be sticky immediately after drying, and after 8 days it must remain deep black when washed with water and with alcohol (85 and 50 p.c.). (2) Iron-gall 'writing inks' must contain at least 18 grams of gallotannic and gallic acids, and at least 2·6, and not more than 4 grams of iron per litre (ratio 4·5 : 1 and 6·75 : 1). In other respects they must comply with the requirements of 'documentary inks.' Inks of Group (*b*) are not officially tested.

Analysis of inks.—The proportion of gallotannic and gallic acids is determined by shaking the sample with ethyl acetate and weighing the residue left on evaporating the extract. The residue is regarded as gallotannic and gallic acids when 0·1 gram thereof absorbs, in the presence of 2 grams of sodium bicarbonate, at least 0·5 gram of iodine. If less iodine is consumed, the ink is not up to the official requirements. Hinrichsen (Chem. Zeit. 1913, 36, 275) discusses the reasons for the changes from the official regulations of 1888, and gives the following details of the methods of applying the official tests :—

Determination of gallotannic and gallic acids.—10 c.c. of the ink are mixed with 10 c.c. of concentrated hydrochloric acid, and the mixture shaken with successive portions of 50 c.c. of ethyl acetate in Rothe's shaking apparatus, until the aqueous layer gives no reaction for gallotannic or gallic acids after treatment with sodium carbonate and addition of ferric chloride and ferrous sulphate. The ethyl acetate extract is shaken several times with semi-saturated potassium chloride solution (10 c.c. each time), to remove iron salts, and then evaporated *in vacuô*, and the residue is taken up with a little water, transferred to a weighed crucible, and dried at 105°–110° or, preferably, *in vacuô* at about 60° until constant in weight. In determining the iodine absorption about 0·1 gram of the residue is mixed in a stoppered flask with 2 grams of sodium bicarbonate and 25–50 c.c. of a solution of iodine (about 50 grams per litre), and the flask closed and allowed to stand over night, after which the unabsorbed iodine is titrated with standard thiosulphate.

Iron.—10 c.c. of the ink are evaporated to dryness, and the residue ignited until free from carbon and then heated with 1–2 c.c. of hydrochloric acid (sp.gr. 1·124) until dissolved. The solution is treated with 1–2 c.c. of chlorine water and evaporated to dryness, the residue treated with 0·5 c.c. of strong hydrochloric acid to dissolve basic iron salts, and the solution cooled and diluted with 20 c.c. of water. About 1 gram of potassium iodide is then added, and the separated iodine titrated with $N/10$-thiosulphate solution, the liquid being meanwhile rapidly warmed to 55° to promote the separation of iodine.

Testing the writing.—Pieces of standard paper are stretched in a frame inclined at an angle of 45°, and a definite amount of ink made to flow down them from a pipette fixed in a special position with regard to the paper. At the same time a parallel test is made upon the same papers with Schluttig and Neumann's standard iron-gall ink containing 23·4 grams of gallotannic acid, 7·7 grams of crystalline gallic acid, 30·0 grams of ferrous sulphate, 10·0 grams of gum arabic, 2·5 grams of hydrochloric acid, and 1·0 gram of phenol per litre. This ink is allowed to stand for at least 4 days at 10°–15°, and decanted from any deposit. For comparison in the test it is coloured with a suitable dyestuff to match the ink under examination. The paper with the colour strips of the two inks upon it is exposed to the air for 8 days in diffused daylight, and is then cut horizontally into strips which are immersed in water, 50 p.c. alcohol and 80 p.c. alcohol respectively. No perceptible bleaching of the ink should take place (J. Soc. Chem. Ind. 1913, 32, 281).

For the American standards for iron writing, duplicating, and cancelling inks, their composition, manufacture, and methods of testing, *see* Circular No. 95, U.S.A. Bureau of Standards, Abstr. in Analyst, 1921, 61.

Ink powders are very little used but can easily be made either by cautiously evaporating an ordinary ink to dryness and powdering the residue, or by mixing the carefully dried and powdered ingredients in the proportions used for the fluid ink.

Indelible or safety inks. Compositions passing under these names consist of finely divided carbonaceous substances, such as Indian ink or lampblack, held in suspension in a glutinous or resinous liquor. They are devised so as to resist the action of strong acid or alkaline solutions. An ink having these properties may be made of Indian ink rubbed into ordinary writing ink.

A suspension of lampblack in sodium silicate solution makes an excellent safety ink, but has the disadvantage that it must be kept in airtight bottles.

Vanadium ink is prepared very simply by adding a small proportion of ammonium vanadate to a filtered decoction of galls. It is a deep black ink, which flows freely from the pen and cannot be removed without destruction of the paper.

Copying ink. Any ink which retains enough solubility to give an impression from the written sheet on to a sheet of damp paper may be used for copying. Runge's chrome ink described above may be so used. Other logwood inks and ferrous gallate inks being soluble only until oxidised by exposure to the air, require the addition of some substance which forms a glaze, arresting the action of the air. This glaze must be soluble when brought into contact with the damped copying paper; the pigment is then freed so as to produce the impression. Such substances are gum arabic, gum Senegal, dextrin, and glycerol. Where several copies are required, the ink employed should contain more staining matter in proportion.

Hektograph inks are used to give a large number of copies, and must therefore contain a powerful colouring matter. The original is written on ordinary paper with the ink and is laid face-down on a sheet of a composition of glue and glycerol (about 1 : 5) until the ink has been absorbed into the surface of the composition.

By applying sheets of paper with slight pressure, 60 to 100 copies can then be obtained.

A typical ink contains: water-soluble blue 10 parts, glycerol 10 parts, and water 50–100 parts.

Dyes not easily soluble in water or glycerol are first dissolved in alcohol and then mixed with the other ingredients. Thus a red hektograph ink may contain: magenta 20, alcohol 20, acetic acid 5, gum 20, and water 40; or magenta 10, alcohol 10, glycerol 10, and water 50.

Red ink was formerly prepared from Brazil wood or extract of Brazil wood, with the addition of alum or stannous chloride: *e.g.*

(1) Brazil wood, 280 parts; tin-salt, 10 parts; gum, 20 parts; boiled with 3500 parts of water and evaporated down until the proper depth of colour is attained.

(2) Extract of Brazil wood, 15 parts; alum, 3 parts; tin-salt, 2 parts; tartaric acid, 2 parts; water, 120 parts.

Cochineal or carmine inks are prepared by boiling cochineal in water, precipitating the colour with alum and tin salt and dissolving this carmine in the requisite amount of strong ammonia. Another method is to dissolve 2 parts of ammonium carbonate in 200 parts of water and macerate for 3–4 hours with 40 parts of cochineal and 2 parts of alum.

Most of the red inks now used are solutions of magenta or eosin in water, together with a little gum. Glycerol also is added if the ink is to be used for copying.

Blue ink. Prussian blue is the colouring matter commonly employed. The pigment is placed in an earthen vessel, and either strong hydrochloric acid, nitric acid, or sulphuric acid is added to it. After the mixture has remained 2 or 3 days, much water is added, and after settling, the supernatant liquor is drawn off from the sediment. This sediment is well washed until all traces of iron and free acid disappear from the water, after which it is dried and mixed with oxalic acid in the proportion of 8 parts of Prussian blue to 1 part of acid. The pigment being now soluble in water, so much of this latter is added as will bring it to the required intensity.

An excellent blue ink can be made by dissolving 10 parts of indigo-carmine and 5 parts of gum in 50–100 parts of water. Solutions of blue aniline dyes may be used, but are easily effaced by bleaching agents and fade on exposure to light.

Inks of other colours can be made from decoctions of dyestuffs mixed with alum (used as a mordant) and gum Senegal or gum arabic; as, *e.g.*, brown ink from catechu or logwood, to which a little potassium dichromate is added; violet and purple inks from logwood with a small admixture of chloride of tin or of alum; yellow ink from gamboge, &c., &c. Aniline colours also offer a selection of tints for this purpose.

Gold and silver inks are *prepared from gold and silver*, or from cheaper substitutes such as bronze powder and Dutch leaf. The leaf metal mixed with honey is carefully ground down to the finest possible condition; it is then well washed and dried. A medium is furnished by a preparation consisting of 1 part of pure gum arabic and 1 part of soluble potash glass in 4 parts of distilled water. As a rule, 1 part of the powder is sufficient for 3 or 4 parts of the medium.

Imitation silver ink is best made by rubbing up aluminium foil or powder with gum.

Sympathetic, Diplomatic, or **Secret inks.** These preparations are devised to trace words or figures which are invisible when written but which become visible when subjected to heat or appropriate chemical reagents. Examples:—A weak infusion of galls is colourless on paper, but becomes black when moistened with a solution of copperas; and if a weak solution of copperas be used, the writing will be invisible, till the paper is moistened with a weak solution of galls. Equal parts of copper sulphate and sal ammoniac dissolved in water form a colourless ink, the writing of which turns yellow on the application of heat. Weak solutions of silver nitrate or of auric chloride when exposed to the sunlight become dark brown and purple respectively. Solutions of cobalt chloride or nitrate give tracings which become green or blue when heated and disappear again as the paper cools.

Ink for indiarubber stamps. The following preparation produces ink adapted for this purpose. It does not easily dry upon the pad, and is readily taken up by the paper:—Aniline colour in solid form (blue, red, &c.), 16 parts; boiling distilled water, 80 parts; glycerol, 7 parts. The colour is dissolved in the water, and the other ingredients are added whilst agitating. The '*carbon papers*' used for giving two or more copies of written or typed matter are coated on one side with a mixture of yellow wax and tallow containing a suitable pigment such as lampblack or Prussian blue, or some aniline colour.

Ticket-writer's ink is made of good black ink, with liquid gum added to produce a gloss.

Ink for writing on glass is a solution of gum arabic in strong hydrofluoric acid coloured with some matter which can withstand the acid: cudbear is used for this purpose.

For enamelled cards ordinary printing ink is mixed with a few drops of equal parts of copal varnish and mastic varnish.

Lithographic ink ought to conform to the following requirements. It should be flowing on the pen, not spreading on the stone; capable of forming delicate tracings, and very black to show its delineations. The most essential quality of the ink is to sink well into the stone, so as to reproduce the most delicate outlines of the drawing and to afford a great many impressions. It must therefore be able to resist the acid with which the stone is moistened in the preparation without letting any of its greasy matter escape.

Lithographic ink may be prepared as follows:—Mastic (in tears) 8 oz., shellac 12 oz., Venice turpentine, 1 oz.: melt together; add of wax 1 lb., tallow 6 oz.; when dissolved, add *further of hard tallow soap in shavings 6 oz.*; and when the whole is perfectly incorporated, add of lampblack 4 oz.; lastly, mix well, cut in moulds, and when cold cut it into square pieces.

Another recipe is as follows:—Melt together wax, 18 parts; soap, 18 parts; shellac, 14 parts; resin, 6 parts; and tallow, 10 parts. Then stir in 2 parts of india-rubber dissolved in 5 parts of oil of turpentine, and 6 parts of lampblack. The whole is heated till the smell of turpentine has nearly disappeared and is then cast into sticks.

Autography is the operation by which a writing or a drawing is transferred from paper to stone. For autographic ink:—White wax 8 oz., white soap 2 oz. to 3 oz.; melt, and add lampblack 1 oz.; mix well, heat strongly, and add shellac 2 oz.; again heat strongly and stir well together. On the mixture cooling pour it out as before. With this ink lines may be drawn of the finest and fullest class, without danger of its spreading; and the copy may be kept for years before being transferred. These inks are rubbed down with a little water in the same way as Indian ink.

Printing ink. Ink prepared for use with type, copper-plates, &c., is composed of a vehicle and pigment. The chief properties required in a good printing ink are:—

(1) A perfectly uniform syrupy consistency.

(2) Must be easily transferred from the ink-rollers to the type, and from the type to the paper.

(3) Must not smudge types, and must be easily washed off them with printer's lye.

(4) The ink must not dry so quickly as to set on types or rollers, but must not dry so slowly on the paper as to hinder folding, &c., of sheets.

(5) When dry, the ink must not set off from the paper on to anything with which it comes in contact.

(6) The printed characters should not show a greasy margin.

(7) The ink should not have a strong smell.

The ink which most nearly fulfils all these requirements is composed of the finest quality of lampblack incorporated with a pure linseed oil varnish. The demand for cheap inks for the printing of newspapers and cheap books has been met by using cheaper qualities of lampblack and substituting for the varnish various compositions of oils and resins with soap, which may or may not contain a proportion of linseed oil.

The linseed oil varnish used for good ink was formerly prepared by heating a quantity of linseed oil in a boiler until the vapour evolved could be ignited. A light was then applied and the whole allowed to burn for about half an hour, until a trial showed that the oil was of the right consistency. The practice of burning the oil gave a dark-coloured product and has now been discontinued.

The present practice is to heat the oil to about 380° to 400°, taking every precaution to avoid its ignition. The boiler is provided with a closely fitting lid or, better, with a cover of wire-gauze, which extinguishes a flame while allowing the vapours to escape.

Provision is made for lifting the boiler from the fire or withdrawing the fire from the boiler, or, in some cases, for running off the oil into a cold vessel. A gutter round the furnace above the fire-door prevents any chance of the oil reaching the fire, even should it boil over the top of the pot. In some modern plant the oil is heated by means of superheated steam. A varnish so prepared is insoluble in water or alcohol, but it mingles readily enough with fresh oil and unites with mucilages into a mass diffusible in water in an emulsive form. The oil loses from one-tenth to one-eighth of its weight by boiling into the thick varnish (Watts).

An average letterpress ink may be made by reheating a varnish produced as above and adding for each gallon of the original oil 4 lbs. resin and 1 lb. brown soap in slices. This is then mixed with the requisite quantity of pigment—rather less than ⅓ of its weight in the case of lampblack—and the whole thoroughly ground and incorporated in a suitable machine, usually between rollers of polished granite or steel, as in Lehmann's apparatus. The presence of soap in the ink causes it to 'lift' well, i.e. to be completely transferred from the type to the paper. The following recipes represent vehicles of a cheaper class:—

Linseed oil and resin vehicle.—Resin 50, boiled linseed oil 100, resin soap 10, partly boiled oil, 6 parts by weight.

Resin oil vehicle.—Resin oil 50, resin 50, boiled linseed oil 50, resin soap 5, thin boiled linseed oil 6 parts.

Cheap mineral oil vehicle.—Resin is dissolved in about an equal weight of heated mineral oil (petroleum) of sp.gr. 0·880–0·920 (Wass, Fr. Pat. 322298, 1908).

Composition vehicles.—5 kilos. Venice turpentine, 15 kilos. castor oil, and 1 kilo. white wax, mixed at 100° (Knecht). 9 kilos. thick turpentine, 10 kilos. soft soap, and 4 kilos. oleine, mixed hot (Rösl).

The lampblack used is of various qualities according to the price of the ink. The proportion used is just sufficient to give a full black impression, and this is less with the better qualities of lampblack. The ink for rotary machines contains about 28 p.c. of lampblack, that for high-speed newspaper printing about 24 p.c., that for book-printing about 21 p.c., and that for illustration work about 19 p.c. with 2 p.c. of Prussian blue and 1 p.c. of indigo.

Brackenbusch's inks consist of 25 parts paraffin oil, 45 parts of fine colophony, and 15 parts of lampblack. The amount of colophony is reduced in soft inks for high-speed work.

It has been proposed to use oxides of iron or manganese as black pigments for printing inks, in which case the paper could be bleached and subsequently re-made into white paper. This cannot be done with the lamp-black inks now used (*see e.g.* Fireman, U.S. Pat. 802928, 1905).

It is said that so marvellously thin is the layer of ink on small type that one pound weight even of cheap newspaper ink will cover no less than 7000 square feet of type matter.

Coloured printing inks. These inks are made from the varnishes above described by the addition of dry colours, taking great care that the colours are thoroughly well ground and assimilated with the varnish, since lumps of any kind not only clog the type but alter the tint. Some tints which are exceedingly light will require an admixture of white powder to give the necessary body to the ink.

The following pigments are eligible for incorporation in printing inks:—

White.—Heavy spar (barium sulphate) and zinc white.

Red.—Orange lead, vermilion, burnt sienna, Venetian red, Indian red, lake vermilion, orange mineral, rose pink, and rose lead.

Yellow.—Yellow ochre, gamboge, and lead chromate.

Blue.—Cobalt, Prussian blue, indigo, Antwerp blue, Chinese blue, French ultramarine, and German ultramarine.

Green.—Usually mixtures of yellow and blue, but sometimes chrome green, cobalt green, emerald green, or *terre verte*.

Purple.—A mixture of those used for red and blue.

Deep brown.—Burnt umber with a little scarlet lake.

Pale brown.—Burnt sienna: a rich shade is obtained by using a little scarlet lake.

Lilac.—Cobalt blue with a little carmine added.

Pale lilac.—Carmine with a little cobalt blue.

Amber.—Pale chrome with a little carmine.

Pink.—Carmine or crimson lake.

Shades and tints.—A bright red is best got from pale vermilion with a little carmine added; dark vermilion when mixed with the varnish produces a dull colour. Orange red and vermilion ground together also produce a very bright tint, and one that is more permanent than an entire vermilion colour. Cheaper substitutes are orange mineral, rose pink, and red lead. Lead chromate makes the brightest colour. For dull yellow, use yellow ochre. Indigo is excessively dark, and requires a good deal of trouble to lighten it. It makes a fine showy colour when brightness is not required. Prussian blue is useful, but it dries very quickly, hence the roller must be frequently cleaned. The objection to Prussian, Antwerp, and Chinese blues, is that they are hard to grind and likely to turn greenish with the varnish when used thin. For green any of the yellows and blues may be mixed. The varnish itself having a yellow tinge will produce a decidedly greenish tint with a small quantity of Antwerp blue. Emerald green is got by mixing pale chrome with a little Chinese blue, and then adding the mixture to the varnish until the tint is satisfactory.

In using painter's colours it is advisable to avoid as much as possible the heavy ones. Some colours require less oil in the varnish than others. For the comparative permanence of colouring matters, *v.* PIGMENTS. For methods of analysis, *see* Tuttle and Smith, (J. Ind. Eng. Chem. 1914, 6, 659).

A bronze of changeable hue may be given to inks with the following mixture (Southward):—Gum shellac 1½ lbs. dissolved in one gallon of 95 p.c. alcohol or Cologne spirits for 24 hours. Then add 14 oz. aniline red. Let the mixture stand for a few hours longer, when it will be ready for use. When added to good blue, black, or other dark ink, it gives a rich hue to it. The quantity must be carefully apportioned.

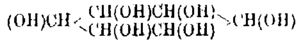
Bronzing The production of printed matter having the colour and lustre of gold or silver, is carried out by printing with a varnish which remains 'tacky' for a time, and then dusting over the whole surface with bronze powder or aluminium powder or similar substances. The powder adheres only to the varnish and thus produces the desired effect.

Such a varnish may be produced by melting into a good linseed oil varnish sufficient beeswax to give it the consistencey of lard or tallow. (*See* Ure's Dict. of Arts, Manufactures, &c.; Cooley's Cyclop. of Practical Receipts; Lehner's Ink Manufacture; Southward's Practical Printing; Noble's Principles and Practice of Colour Printing; L. E. Andes' Oil Colours and Printer's Inks; and Seymour's Modern Printing Inks.)

INKANI FAT. A fat obtained from the seeds of the East African tallow tree, *Steatodendron Stuhlmannii* (Engl.).

INOSIC ACID, INOSINE *v.* CARNINE.

INOSITOL (*Inosite*). A number of natural substances having the composition of cyclic polyalcohols, *e.g.* hexahydroxy*cyclo*hexanes $C_6H_6(OH)_6$, are often classed with the carbohydrates since they have the same formula, taste sweet, occur along with them in nature, and possibly have been formed from them by the junction at the ends of the six carbon chain, although such transformation has never been realised in the laboratory. Typical of the class is inositol. No less than nine stereoisomeric inositols:



$$(\mathrm{OH})\mathrm{CH}<\begin{matrix}\mathrm{CH(OH)CH(OH)}\\\mathrm{CH(OH)CH(OH)}\end{matrix}>\mathrm{CH(OH)}$$

are possible, of which seven are inactive and two optically active and enantiomorphic. Four of these have been described, viz. optically active *d*- and *l*-inositol, and inactive inositol, and cocositol or scyllitol. Similar pentahydroxy*cyclo*hexanes are likewise found in plants. These are *d*- and *l*-quercitol.

The formation of **furfural** on distillation of *meso*inositol with phosphoric anhydride in a copper vessel (Neuberg, Biochem. Zeitsch. 1908, 9, 551) is the only instance in which a complex substance has been obtained common to both the carbohydrates and inositol.

d-**Inositol** (*matezodambose*) is prepared by demethylation (boiling with concentrated hydriodic acid) of the naturally occurring methyl ether, pinitol. It crystallises in anhydrous prisms, m.p. 247°–248°, $[\alpha]_D +65°$ without mutarotation and forms hexacetyl and hexabenzoyl derivatives.

The methyl ether, **Pinitol** (*pinite*) $C_7H_{14}O_6$, also called *matezite* and *sennite* was discovered in the resin of the Californian *Pinus lambertiana* (Dougl.) (Berthelot, Compt. rend. 1856, 41, 392). It occurs in the residues of the manufacture of coniferin, in senna leaves, and in the liana of Madagascar rubber (*mateza roritina*). It crystallises in colourless rhombs, m.p. 186° $[\alpha]_D +65{\cdot}5°$. The structure of pinitol was established by Maquenne (Compt. rend. 1889, 109, 812).

l-**Inositol** was obtained by Tanret (Compt. rend. 1889, 109, 908) by demethylation of quebrachitol. It crystallises in needles; m.p. 247 $[\alpha]_D -65°$.

The methyl ether, **Quebrachitol** (quebrachite) occurs in quebracho bark. It crystallises in prisms; m.p. 186 $[\alpha]_D -80°$.

r-**Inositol,** obtained by mixing the *d*- and *l*-isomerides in equal quantities, is optically inactive, m.p. 253°. Tanret (Compt. rend. 1907, 145, 1196) has obtained both racemic- and *meso*-inositol from fresh ripe berries of mistletoe.

Meso- or *i*-**Inositol** (*dambose, nucite*) is widely distributed in both plants and animals. It occurs in muscles, in the heart, lungs, and liver, in beef and horseflesh, and in the urine in cases of Bright's disease. In plants, it is found in beans, peas, &c., in the leaves of asparagus, oak, ash, walnut, &c., in all parts of the grape vine and hence in wines and in fungi. The chief source is the leaves of the walnut tree (Tanret and Villiers, Compt. rend. 1877, 84, 393; 1878, 86, 486), but very much larger quantities are afforded by mistletoe. It may also be prepared from cochineal mother liquors. It crystallises in bunches of needles, m.p. 225°, and does not reduce Barreswil's solution. Yeast is without action, but certain fungi decompose it. The hexacetate forms monoclinic plates, m.p. 212°. Hugo Muller (Chem. Soc. Trans. 1907, 91, 1780) has described and measured the crystals of the monobromopentacetate, minute crystals, m.p. 240°, the dibromotetracetate, broad transparent prisms, m.p. 140°, and scaly crystals, m.p. 235°; also of inositoldibromohydrin, m.p. 210°.

When inositol is evaporated with nitric acid almost to dryness and then again carefully evaporated with ammoniacal calcium chloride, a rose-red coloration is obtained which enables 0·0005 gram to be detected with certainty (Scherer, Annalen, 1850, 73, 322). With ammoniacal strontium acetate, a still more delicate violet coloration is obtained.

The monomethyl ether, **Bornesitol**, occurs in Borneo rubber; it forms rhombic prisms, m.p. 199°–203°.

The dimethyl ether, **Dambonitol**, is found in Gabon rubber; it crystallises in hexagonal prisms, m.p. 195°.

Phytin, which is present in many plant seeds, *e.g.* cotton seed meal, oats, maize, and has been isolated from rice bran, is a magnesium calcium compound of inositol phosphoric acid (Winterstein, Zeitsch. physiol. Chem. 1908, 58, 118).

Phytic acid from maize meal is a yellow viscous mass which decomposes when heated with water at 155° into phosphoric acid and inositol. Inositol tetra- and pyrophosphoric acids have been synthesised by Anderson (J. Biol. Chem. 1912, 11, 471; 12, 97). Contardi (Gazz. chim. ital. 1912, 42, 408) obtained the hexaphosphate by the action of phosphoric acid on inositol at 120°–130° in absence of air. This is regarded as identical with the phytin found in seeds (*cf.* Clarke, Chem. Soc. Trans. 1914, 535). *See* art. PHYTIN.

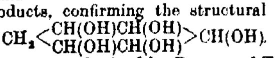
New forms of inositol are produced by the action of hydrochloric or hydriodic acids in acetic acid solution upon inositol (Hugo Muller, Chem. Soc. Trans. 1912, 101, 2383).

Iso-*inositol* is crystalline, m.p. 24[illegible]°–250°, readily soluble in water, insoluble in ether, benzene, or chloroform, or alcohol, but soluble in boiling 50 p.c. aqueous alcohol. It has a very faint sweet taste. Its *hexa-acetate* melts at 112°, and its *tetrabenzoate* at 213°.

ψ-Inositol is an amorphous or microcrystalline mass, very soluble in water, but very sparingly so in alcohol. Its nitrate is moderately explosive.

Scyllitol (scyllite) $C_6H_{12}O_6$, discovered by Staedler and Friedrichs (J. pr. Chem. 1858, (i) 73, 48) in various organs of the *Plagiostomi* (dog-fish) has been investigated by J. Müller. It is inactive, crystallises in hard lustrous monoclinic prisms, m.p. above 339° and is sparingly soluble in water. It gives Scherer's reaction and forms a hexacetyl derivative.

Cocositol (cocosite) $C_6H_{12}O_6$, was discovered by Hugo Muller in the leaves of *Cocos nucifera* (Linn.) and *Cocos plumosa* (Hook.) (Chem. Soc. Trans. 1907, 91, 1767). It crystallises from water in large transparent lustrous monoclinic crystals, m.p. about 345°–350°, and is optically inactive It forms a hexacetate, giving prismatic crystals, m.p. about 300°, also a benzoate and nitrate. It gives the red coloration characteristic of inositol (Scherer's reaction). H. Muller (Chem. Soc. Trans. 1912, 101, 2383) has shown scyllitol, quercine from acorns, and cocositol to be identical, and names all three scyllitol; the occurrence of this substance in two such different organisms as the cocoa-nut palm and the dog-fish is most remarkable.

d-**Quercitol** $C_6H_{12}O_5$ is found in the acorn and in minute quantity in the cork and bark of the oak. Hugo Müller (Chem. Soc. Trans. 1907, 91, 1766) has also obtained it from the leaves of *Chamærops humilis* (Linn.), the only European representative of the palm family, which was formerly used like esparto for making paper. The leaves contain 1·35 p.c. of quercitol. They are crushed, extracted with boiling water, and the extract precipitated first with neutral and then with basic lead acetate. The lead in solution is removed and the filtrate evaporated until crystals appear It crystallises in prisms, m.p. 234° $[\alpha]_D+20{\cdot}16°$. It is not fermentable and forms acetyl and similar esters, showing that it contains five hydroxyl groups. Potassium permanganate oxidises it to malonic acid and other products, confirming the structural formula as  $CH_2{<}\begin{matrix}CH(OH)CH(OH)\\CH(OH)CH(OH)\end{matrix}{>}CH(OH)$.

l-**Quercitol** was obtained by Power and Tutin (Chem. Soc. Trans. 1904, 85, 624) from the leaves of *Gymnema sylvestre* (R. Br.). It crystallises in prisms from water or needles from alcohol, m.p. 174° $[\alpha]_D-73{\cdot}9°$, and forms penta-acetyl and penta-benzoyl derivatives. On oxidation with potassium permanganate, malonic acid is formed; with sodium hypobromite, the product is diketotrihydroxyhexahydrobenzene $C_6H_5O_2(OH)_3$. It is not the optical antipode of *d*-quercitol.

Quercitol contains 4 asymmetric groupings, and therefore 8 optically active and two unresolvable inactive modifications are possible.

E. F. A.

INSECTICIDES *v.* PLANT-SPRAYS.

INSIPIN. Trade name for the glycollic ester of quinine sulphate.

INTERFEROMETER. The interferometer, or rather the interference refractometer, is an instrument for measuring small differences in refractive power between two gases or two liquids; this it does with much greater refinement than other forms of refractometer, and consequently it can be used to measure small differences in composition between two gaseous mixtures or between two solutions, and in one of its forms it has been used to find the refractive indexes of new gases by comparison with air. It takes advantage of the set of bands produced by the phenomenon of interference and employs such sets as pointers or indexes.

If the white light from a single source is broken up into two beams, and if these are made to unite again either on a screen or as viewed through a telescope, a set of interference bands is observed having a central white band with a series of dark bands to the right and left. These bands are caused by the light waves of the two beams meeting and in some places reinforcing, and in others obliterating one another according as they are in the same phase or in opposite phases. The dark bands are fringed with colour owing to white light being made up of coloured lights of various refrangibilities; if monochromatic light is used only bright and dark bands are seen. The two beams must come from the same source or no bands will be formed. The phenomenon is discussed in textbooks on Light.

Shifting of the central band is observed when a different material is introduced into the path of one beam and not into that of the other; it is on this shifting that the measurement depends. When both beams pass through exactly the same lengths of the same materials their 'optical lengths' are equal and the central band is seen in a certain place, but if a new material with a different refractive index is introduced into the path of one beam, its 'optical length' is now changed and the central band is shifted to a new position. A material of higher refractive power diminishes the velocity of light more than a material of lower refractive power and increases the 'optical length' of the path traversed by the rays. The *optical length* of the path of a ray between two points is equal to the actual distance multiplied by the index of refraction of the material through which it passes. If the ray passes through several materials the total optical length is the sum of the several optical lengths.

Different ways of restoring the central band to its former position are employed in various forms of the instrument and so measuring the difference in refractive indexes, and further there are different methods of effecting the division of the beam of light.

Jamin (Ann. Chim. 1858, [3] 52, 163 and 171) used reflection and refraction in a thick glass plate to separate the beam and send it through two tubes; but Lord Rayleigh, using a modification of an arrangement investigated by Fraunhofer, effected the separation in an easier way.

Rayleigh's Interference Refractometer for Gases.—This was used by Lord Rayleigh when determining the refractive power of argon and helium by comparison with air (Proc. Roy. Soc. 1895–96, 59, 201; 1898–99, 64, 97; also Traver's Experimental Study of Gases, 1901, 292; also Watson Practical Physics, 1906, 343). The way i which it acts can be seen from Fig. 1, bu various forms of it have been described. Th plan adopted is to render the rays of ligh from a slit parallel by means of a collimatin lens, then to divide them into two beams b passing through two narrow apertures, an finally to unite them again by means of telescope in which the interference bands wi be seen. The rays of light from a lamp on th right pass through a very fine vertical slit an are rendered parallel by the lens B. The lam and slit are not shown in the figure. The ray then pass through the two tubes D and E, and on to the two vertical and parallel apertures CC in the cap of a telescope having a lens at Q. These apertures are parallelograms about ¼ inch wide and 1½ inches apart, and are exactly opposite the ends of the tubes. The figure shows the arrangement in plan, the slit and apertures being perpendicular to the plane of the paper. Instead of viewing the bands through the lenses of an ordinary eyepiece, much greater magnification was obtained by employing a glass cylinder, shown at R; it appears there as a circle, since it is perpendicular to the plane of the paper and parallel to the slit and apertures. It was cut from a piece o plate glass, glass rod being unsuitable; it ha the advantage of magnifying the bands i width only. At first a web was used as th reference mark for measuring the shift of th bands, but a much better plan was found to b allowing light from B, travelling not throug but in the air above the two tubes, to form set of reference bands which are stationary an not affected by the materials in the tube Each pair of ends of the tubes is closed by glass plate, the faces of which must be opticall worked so as to be parallel. The appearan in elevation can be gathered from Fig. 2, whic represents the next instrument; it shows how the top half of the beam passes above the tubes and the lower half through them. Each of the tubes D and E has a side tube through which it can be filled, and these side tubes are in connection with mercury manometers with adjustable reservoirs by which the pressure in each tube can be varied and ascertained. The tubes are filled with air and the gas under investigation respectively, and the pressures are adjusted until the central band is brought to a definite position in relation to the reference bands. The pressures in the two tubes are, of course, different when this is attained. Other experiments are made with other pressures, the central band being always brought back to the same position as regards the reference bands. The relative refractivity is calculated from the relation between the pressures in the air tube and in the other gas; the refractivity being $(\mu-1)$, where μ is the index of refraction.

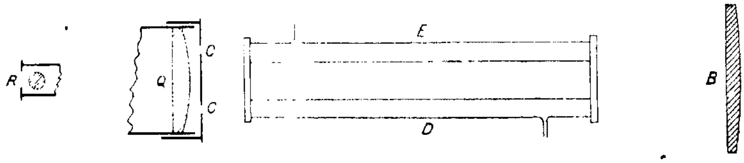


FIG. 1

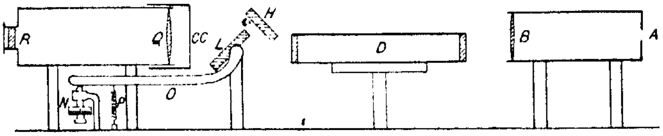


FIG. 2.

Löwe's Interference Refractometer for Liquids and Gases.—An instrument employing Lo Rayleigh's method of dividing the beam, h cylindrical lens, and his plan of using a seco set of bands as a reference mark is described Löwe (Zeitsch. für Instrumentenkunde, 191 30, 321; Zeitsch. Physikalische, 1910, 11, 104 as made by Zeiss. Fig. 2 shows the mode action of the instrument, though not the actu dimensions; A is the slit and B is a collimati lens; the materials under examination a contained in two tubes, D and E, placed side side; of these the near tube D is seen in t figure, which shows the apparatus in elevatio Rayleigh's apparatus could only be used f gases, and required two mercury manomet with accessories to bring the central band ba to the right position; Löwe dispensed wi these by means of a compensator, and made t apparatus applicable for both liquids and gas The compensator is an arrangement of gla plates something like an arrangement used Jamin (*l.c.*). It consists of two glass plat one placed in the path of the beam from each tube and at an angle of about 45° to the beam. One of them, L, is movable about an axis, and can be inclined at a greater or less angle to the beam by means of the lever O, which is moved by the micrometer screw N. The other plate, K, is exactly like L, but is fixed; it is hid by L in the figure and lies in the path of the beam from the further tube E, which is hid by D.

If a ray of light passes through a glass plate, it will traverse the minimum of glass when the plate is perpendicular to the ray, the more the plate is inclined from this position the greater will be the length of glass traversed. Thus by the device described above, when the optical length of the beam coming through the material in the near tube D is less than that of the beam coming through the other tube E, a further inclination of the glass plate L serves to increase the length of glass traversed, and thus the central band can be brought back to the reference band by turning the micrometer screw N. Attached to this screw there is a drum, the graduations on which serve to measure the inclination given to the plate L, and so to estimate the difference in refractive power of the materials in the two tubes.

The upper part of the light from the collimating lens B passes above the tubes and forms the stationary reference bands. On its way it meets the inclined glass plate H which is fixed and serves to direct the light into the telescope RQ. This, as in Rayleigh's apparatus, has two apertures at CC and a cylindrical eyepiece R. Without the plate H the top of the tubes D and E would appear in the eyepiece as a thick dark line, making it difficult to bring the two sets of bands into exact concordance, but the effect of H is to blot out or diminish this line (Rayleigh, Proc. Roy. Soc. 1898–99, 64, 97).

The instrument in the above form is long and suitable for a laboratory bench, but besides this Löwe describes a shorter and less sensitive form. In this, when used for liquids, the tubes or chambers are immersed in a water-bath in order to maintain a uniform temperature in both. Irregularities in temperature interfere with the setting of the bands and reference bands together, and also make the bands crooked (Wolff, Chem. Zeit. 1915, 39, 106).

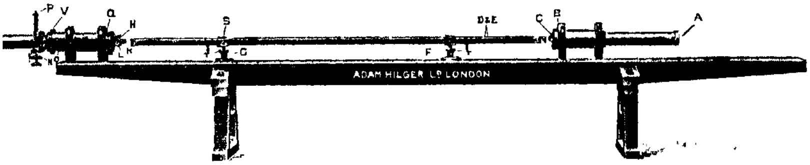


FIG. 3.

An instrument on the plan of the long form is made by Adam Hilger of 75*a*, Camden Road, N.W.1, for use with gases, and is shown in Fig. 3. The lettering corresponds to that of Fig. 2, but the two apertures CC are placed close to the collimating lens B instead of on the telescope QR. Of the further letters, F and G indicate standards supporting the tubes; T and T are nuts for raising or lowering the tube, which can also be adjusted laterally by a screw at S; K is the fixed glass plate and Q is the object glass of the telescope; V is a knurled ring for focussing the telescope, and P is a spring opposing the micrometer screw. The apertures are 4 mm. wide and 12 mm. apart; the two gas tubes are made of brass and are 1 metre long and 1 cm. square in section, and are closed by glass plates with parallel faces. It is claimed that with this instrument settings can be made to less than one-fortieth of a band, and that it is possible to detect the presence of 0·01 p.c. of hydrogen in air, corresponding to a difference in refractive index of 0·000,000,015.

Hilger also makes a much shorter instrument for use with liquids; it has a cell 1 cm. long and the range is about 0·006 instead of about 0·000017, which is that of the long form.

Both long and short forms of the instrument have to be graduated empirically, that is to say, the values corresponding to the readings of the drum have to be found by experiments using liquids and gases of known composition. The tubes are first both filled with the material taken as a standard, the compensator is adjusted so that both sets of bands coincide and the drum is read off. This reading gives the starting-point and has to be deducted from subsequent readings; it may vary a little from day to day. The tube opposite one of the plates is now filled in succession with prepared mixtures containing known additional quantities of the substance it is wished to measure, the compensator is adjusted and read and a table or curve is prepared, by the use of which the amount in a sample under examination can be found. Which tube or chamber to use will depend on which material has the greatest refractive power and also on the way the instrument is made; if the movable plate is inclined away from the lever as in Fig. 2, raising the lever increases the path through glass; but if, as in some instruments, it is inclined towards the lever, raising the lever diminishes the path. It is best that the water used for comparison and for making standard solutions should be parts of the same lot. Several settings and readings of the drum should be made with each portion of liquid or gas tested, and for the greatest accuracy it is advisable to repeat this with other portions of the same lot.

Another way of making a determination is to prepare two mixtures of known strength, one a little stronger and one a little weaker than the sample under examination. The end points are found by testing these mixtures first with both tubes or chambers filled with the same mixture, and then with one mixture alongside the other. Having found the end points, which should not be far apart, the sample is compared first with one mixture and then with the other, and its strength is calculated by interpolation. Using this plan the shifting of the colours described below is less likely to cause difficulty.

Besides Rayleigh's and Löwe's there are other forms of interferometer which are of interest to the physicist rather than to the chemist.

Corrections.—Care must be taken to identify the central white band correctly and not to mistake a side band for it. Further, in using the compensator there is an action, which as the glass plate is more and more moved and as the readings on the drum get higher and higher, shifts colours on to the original central band and makes it harder to identify, and which then whitens in turn first one and then another neighbouring band so that it appears like the original central band. The effects of this action have to be ascertained and allowed for. It is caused by differences in dispersive power between the glass plate and the solutions, so that the corrections vary with the substances in solution and with different instruments. The action is discussed by Marc in Chem. Zeit. 1912, 36, 537, by Valentiner and Zimmer in Ber. Deutsch. Physik. Gesell. 1913, 15, 1301, and by Adams in J. Washington Acad. Sci. 1915, 5, 265, and in J. Amer. Chem. Soc. 1915, 37, 1181, where many directions are given. This correction has also to be considered in the case of Rayleigh's instrument (Valentiner and Zimmer, *l.c.*, p. 1316).

Different intensities of the two black bands in the centre indicate a faulty adjustment of the light.

In other kinds of refractometer it is important to maintain a constant temperature during an observation, as temperature greatly affects refractive power, but with the interference refractometer this is less important, as any variation in temperature affects both tubes, and it is only when temperature has distinctly more effect on the refractive power of the material in one of the tubes than on that of the material in the other tube that a difference can be noticed between observations at different temperatures. It is advisable to make sure that errors due to difference of temperature between that of graduation and that of observation are negligible (Edwards Chem. and Met. Eng. 1919, 21, 762).

It should be noted that the readings on the drum are not in simple proportion to the differences in refractive power. Adams (J. Amer. Chem. Soc. 1915, 37, 1191) gives formulæ for calculating values that are directly proportional; they involve finding a constant for the particular instrument used; but as each instrument is graduated empirically as described above, it is not essential to employ these formulæ.

Edwards (J. Amer. Chem. Soc. 1917, 39, 2382) proposes in the case of gases to prepare calibration tables for the interference refractometer by an experiment with air at different pressures and then by calculation from the known refractive indexes of various gases, but certain points have to be taken into account.

Uses.—The interference refractometer can be used for comparing two liquids or two gases together which differ in that one contains more of a certain known substance than the other, and for ascertaining the amount of this excess. The longer the tubes or chambers containing the materials the greater is the sensitiveness, and the shorter the tubes or chambers the greater is the range of differences that it will determine. Further, the greater the difference in refractive power between the standard substance and the substance to be determined the greater is the sensitiveness; thus when carbon monoxide with refractive index 1·00034, nitrogen with 1·000297, oxygen with 1·00027, dilute air with 1·000293, the sensitiveness is not nearly so great as when hydrogen with 1·000139 is the diluent; in which case it is claimed, as stated before, that 0·01 p.c. of hydrogen in air can be found.

In the case of liquids Adams (J. Amer. Chem. Soc. 1915, 37, 1187) says that with his instrument, using a 4 cm. chamber through which the light was reflected back, and which consequently was equivalent to an 8 cm. chamber, a difference of 2 parts per million of sodium chloride in aqueous solution could be found.

The following applications of the interference refractometer have been made or suggested:

In the case of gases for examining: (1) Air in ventilation systems. (2) Flue gases for boiler control. (3) The gas in airships. (4) Illuminating gas. (5) Ammonia in distillation gases. (6) The gas evaporating from liquid air. (7) Mine air for methane. Kuppers (Glückauf, 1913, 49, 47) gives directions for testing mine air; this and the ordinary air used for comparison should be freed from carbon dioxide and water vapour by means of soda-lime and calcium chloride. If the mine air is deficient in oxygen a correction must be made (Seibert and Harpster, U.S. Bureau of Mines Tech. Paper No. 185, 1918, p. 11). In testing gases by Löwe's instruments the pressure must be the same in both tubes; this can be effected by making them both communicate with the atmosphere during an observation, but with some device to check diffusion.

In the case of liquids: (1) Examination of sea-water, for variations in saltness (Löwe, Annalen d. Hydrographie, 1912, 40, 303). (2) The analysis of colloid solutions and the investigation of the phenomena of adsorption (Marc, Chem. Zeit. 1912, 36, 537). (3) The determination of the efficiency of filtering materials in water works (Marc, *l.c.*). (4) Standardising solutions for volumetric analysis. (5) Determining potassium and sodium in a mixture of their sulphates (Adams, J. Amer. Chem. Soc. 1915, 37, 1194). (6) Testing the activity of diastase and yeast (Wolff, Chem. Zeit. 1915, 39, 105 and 197).

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H. H. R.

INSECT WAX *v.* Waxes.

INSIPIN. Diglycollic acid ester of quinine.

INTENSIFIERS *v.* Photography.

INTRAMINE. Trade name for di *o*-aminophenyl disulphide, used in the treatment of syphilis.

INULA CAMPHOR *v.* Camphors.

INULIN *v.* Carbohydrates.

INVAR. A steel containing 35·4 p.c. nickel having an extremely low coefficient of thermal expansion (*v.* Nickel).

INVERTASE (*Sucrase*). Invertase is the enzyme which hydrolyses or inverts sucrose to dextrose and lævulose. It is present in all yeasts except *S. octosporus*, *S. capsularis*, and *S. membranæfaciens* (Hans.), and is extremely active. According to O'Sullivan and Tompson (Chem. Soc. Trans. 1890, 57, 834), whose contribution to the subject is still a classic, it can hydrolyse 200,000 times its weight of sucrose, and probably this figure is much understated. As is the case with other enzymes, but little is known of its nature.

O'Sullivan purified invertase by fractional precipitation so long as it remained active, and found that the proportion of carbohydrate increased. He identified this as mannose, as was also done by Koelle (Zeitsch. physiol. Chem. 1900, 29, 429). A very pure preparation was obtained by Osborne (*ibid.* 1899, 28, 399) which gave none of the protein reactions, except precipitation by copper sulphate, lead acetate, and phosphotungstic acid; it gave the biuret, xanthoprotein, and Millon's test faintly, and could not be freed completely from carbohydrate. It also always contained nitrogen and ash. Salkowski (Zeitsch. physiol. Chem. 1909, 61, 124) considers that invertase does not contain carbohydrates and that the yeast gum which accompanies it is an impurity. *Cf.* Willstatter and Racke, Annalen, 1921, 425, 1.

According to Mathews and Glenn (Bio-Chem. J. 1911, 9, 29), the most active preparation contains about 2 p.c. of ash and 2·2 p.c. of nitrogen. It consists of a gum and a nitrogenous portion yielding 70–76 p.c. of mannose on hydrolysis. These authors consider invertase to consist of a union of an inactive colloidal gum with an active protein ferment; by the action of acid, the ferment is freed from the carrier and rendered active.

Mathews and Glen (J. Biol. Chem. 1911, 9, 29) consider that as ordinarily prepared invertase is a combination of a protein and a mannosan. All attempts to free the protein from the gum and retain enzymic activity were a failure. The parallelism between activity and nitrogen content is taken as indicating that the active substance is a protein.

Nelson and Born (J. Amer. Chem. Soc. 1914, 36, 393) find that highly purified invertase does not show the protein reactions until after hydrolysis with dilute sulphuric acid, indicating that the properties of the protein are effectually masked in the invertase itself.

Invertase appears to be effective in all cases where dextrose and lævulose are united, even when a third sugar molecule is attached to these. Thus it hydrolyses raffinose, gentianose, melicitose, and stachyose, splitting off lævulose in each case.

Invertase is of common occurrence in the vegetable kingdom; it is present in buds, flowers, and leaves of the higher plants and in numerous mould fungi. It is not so widespread in the animal body as maltase, being practically limited to the mucous membranes of the alimentary canal.

The laws regulating the velocity of invertase action are dealt with elsewhere (*v.* Fermentation and Hydrolysis).

It is very sensitive to the minutest quantities of alkali, which retard or stop its action, and for this reason its action is accelerated by dilute acids or acid salts, although probably, like diastase, it is most active in truly neutral solution. Quantitative work with invertase must be carried out in hard glass vessels and with solutions which have been stored and measured in such vessels. It is the neglect to avoid alkaline impurity which has occasioned many of the controversial statements in the extensive literature relating to this subject.

The rate of action is much influenced by temperature: 55°-60° being that of maximum activity, beyond which it becomes weakened by heat (*see* also papers by Euler, Zeitsch. physiol. Chem. 1910 and 1911). It is destroyed between 65° and 70°. The power of the enzyme to resist heat is considerably increased by the presence of sucrose: according to O'Sullivan, it will withstand a temperature 25° higher.

An active solution of invertase is readily obtained by extracting dried yeast with water or by shaking up living yeast with chloroform water. A very active permanent preparation may be prepared by setting aside washed pressed yeast with a little water to autolyse at 37° for a few days. The liquid is filtered and alcohol added a few cub. cm. at a time to the filtrate so as to keep the precipitate in a granular form. The liquid is decanted, the precipitate washed first with a little 60 p.c. and then with 80 p.c. alcohol and at once dissolved in a minimum quantity of water. The precipitation process may be repeated and the final product dissolved clear in the smallest quantity of water and bottled with a little toluene. This solution, which is of very high activity, may be kept for years without its activity materially changing (*v.* Fermentation).

Investigations made by Euler, and later by Meisenheimer (Biochem. Zeitsch. 1913, 54, 122), have shown that the amount of invertase in yeasts is largely increased by allowing them to remain in contact with various sugars for one or two days. The invertase was prepared from the expressed juice by the acetone method. Under these conditions the zymase content of the yeasts diminished. Invert sugar or fructose caused a larger increase in the invertase than glucose or cane sugar, a fact which is explained on the assumption, previously made by Armstrong, that a fructose-invertase combination is somewhat more stable than the combination of invertase with other sugars, and the ferment is thereby more efficiently guarded against change during the autolysis of the yeast. Euler (Zeitsch. physiol. Chem. 1913, 88, 430) claims that it is the process of fermentation as such, and not the substrate or the products of the reaction, which influences the formation of new invertase. Enzyme formation is closely correlated with the formation of fresh protoplasm.

The hydrolysis of cane sugar by active invertase preparations is complete, and the most careful experiments made by Armstrong (*v.* The Simple Carbohydrates), and later by Hudson and Paine (J. Amer. Chem. Soc. 1914, 36, 1571), have failed to detect any evidence of synthetic activity. E. F. A.

IODALBACID, IODALBIN, IODANISOL, IODEIGONS, *v.* Synthetic drugs.

IODEMBOLITE *v.* Embolite.

IODGLIDIN, IODIN, *v.* Synthetic drugs.

IODINE. Symbol I. At.wt. 126·93. This element was discovered in 1812 by Courtois in the mother liquor of kelp. The discovery was first announced to the French Institute in 1813. The properties of the new element were further investigated by Clement and Desormes, Gay-Lussac, and Davy.

Iodine is a crystalline solid of greyish-black colour and bright metallic lustre resembling plumbago. Its sp.gr. is 4·948. It is obtained by sublimation in brilliant rhomboidal plates, or in elongated octahedrons belonging to the trimetric system. In very thin plates it transmits light of a red colour. It melts at 114·15°, and boils at 184·35° (Ramsay). It volatilises at ordinary temperatures spontaneously in the air, diffusing an odour resembling chlorine. It is sometimes employed in this way in hospitals as a disinfectant. Its vapour pressure at 50° is 2·15 mm.; at 60°, 4·29 mm.; at 70°, 8·20 mm.; at 80°, 15·09 mm.; at 90°, 26·78 mm. (Baxter and Grose, J. Amer. Chem. Soc. 1915, 37, 1061). The vapour has an intense blue or rich violet colour, and is one of the heaviest of all known gases, having a sp.gr. of 8·801. A stratum 4 inches thick presents a black mass quite impervious to light. Heated above 700° the sp.gr. of the vapour begins to diminish until at 1700° it is half that at 700°, and the vapour is monatomic. It is very slightly soluble in water, requiring about 3616 parts for solution at 18°. It is soluble in chloroform, bromoform, carbon disulphide, light petroleum, and benzene, forming violet solutions; also in ethyl, methyl, and amyl alcohols, and in ether and glycerol, forming brown solutions. It is very soluble in potassium iodide, of which 1 part in 2 parts of water will dissolve 2 parts of iodine, forming potassium triiodide KI_3. In reactions it resembles chlorine and bromine, but is less energetic, and is displaced by these elements from its compounds with hydrogen and the metals. It has a strong affinity for most of the metals, and in the presence of water, attacks and dissolves gold. The most characteristic reaction of free iodine is the dark blue compound formed with starch; this test is extremely sensitive, and will reveal the presence of one-millionth part in any liquid containing it. Another characteristic reaction is to liberate the iodine from a solution by nitrosulphuric acid, and dissolve it out by carbon disulphide; this affords an accurate and easy method of estimating it by the depth of the crimson colour of the solution; it is also extremely sensitive, and well adapted to estimate small quantities of the element.

Isotopes of iodine.—By the method of positive ray analysis, iodine is shown to be a simple element of atomic weight 127 (Aston, Chem. Soc. Trans. 1921, 119, 677).

Iodine in minute quantities is very largely distributed throughout the animal, vegetable, and mineral kingdoms. The thyroid gland of the sheep contains, for example, on the average, when dry, 0·34 p.c. of iodine, or on the fresh gland 0·09 p.c. (Martin, Pharm. J. 1912, 89, 144). As a mineral it occurs in combination with silver, mercury, and lead, in ores from Mexico, Chile, and Spain, with zinc in Silesia, and with lead in South America. It is also found in dolomite from Saxony, in limestone from Montpellier, in shale from Sweden, and in calcium phosphate from France. It exists also in the 'caliche' of Chile in the form of sodium iodate. This is the only mineral source from which it is manufactured, and has been for many years the most important of all the commercial sources.

Many mineral waters contain iodine, notably those of Carlsbad in Bavaria, Hall in Austria, Marienbad in Bohemia, Holberg in Pomerania, Halle in Saxony, Sales in Piedmont, Nix in Savoy, Kreuznach in Galicia, Halse in Java, and Jallien in France. It is also found in the waters of Friedrichshall, Castellamare, Heilbrun, Homburg, Seidchutz, and Vichy; and in this country in those of Leamington, Bonington, Bath, Cheltenham, and Woodhall. It is a valuable remedy in skin diseases. The sea is an abundant source. Iodine is always present in sea-water, but in such a very minute proportion that it is difficult of detection except by operating on large quantities. It has been estimated in the Atlantic at 1 part in 280,000,000 (Stanford). Iodine in organic combination is not found in Atlantic ocean water. According to Winkler (Zeitsch. angew. Chem. 1916, 29, i. 205), the total iodine content of the water is approximately 0·05 mg. per litre. Near the surface where the water is exposed to air and sunlight, the iodate-ion predominates; at a greater depth the relation between the iodate and iodide changes, the proportion of the latter increasing. All fishes and all animal products from the sea appear to contain iodine, but in very minute quantity. The following table shows a few of the marine products in which it has been estimated:—

Cod-liver oil	0·000322	p.c. iodine.
Cod-liver	0·000817	,,
Codfish	0·000160	,,
Herring, salt	0·000650	,,
Whale oil	0·000100	,,
Seal oil	0·000050	,,
Oysters (Portuguese)	0·000040	,,
Prawns	0·000440	,,
Limpets	0·003200	,,
Cockles	0·002140	,,
Whelks	0·008920	,,
Mussels	0·035720	,,
Sponge (Turkey)	0·200000	,,
Sponge (Honeycomb)	0·034000	,,

Nearly all seaweeds or marine algæ contain it. It may be extracted from seaweed by a solution of aluminium sulphate. This when treated with copper sulphate and sulphurous acid or a sulphite yields cuprous iodide. It is present even in the *Zostera marina* (L.) or grass wrack, natural order *Naiadaceæ*, a flowering plant growing only in the sea; but there are some remarkable exceptions. The gelatinous species of algæ, the *Chondrus crispus* (L.) (or Irish moss), and *Gelidium corneum* (Lam.) of British species, and the *Eucheuma spinosum* [(L.) J. Ag.], or *Agar agar* of foreign species, do not contain iodine. The *Enteromorpha compressa* [(L.) Grev.], or common sea grass, when dry has a strong odour of the sea, but does not contain iodine. The salsola or salt wort, *Salsola Kali* (L.), natural order *Chenopodiaceæ*, growing on the seashore, and from which barilla was made, contains no iodine. Some of the algæ are comparatively rich in iodine, and the ash of these plants, known as kelp, for many years formed the only commercial source of this important element. For the distribution of iodine in plant and animal tissues, *see* Cameron, J. Biol. Chem. 1915, 23, 1.

Manufacture.—By far the greater bulk of all the iodine produced is now extracted from the mother liquors of the nitrate works in Chile, but the manufacture of iodine from kelp has for long been carried on in Scotland and in France, and within recent years has been started in Norway and in Japan. Courtois, a saltpetre maker in Paris, who discovered iodine, obtained it from the kelp liquors which were used to furnish the salts of potash required in his manufacture, and this was for many years the only commercial source of iodine. The manufacture was unsuccessful commercially in the hands of the discoverer, and he died in poverty. It was afterwards successfully carried out by MM. Cournerie of Cherbourg, and has continued to be an important manufacture on the Normandy coasts. In this country it was first made on the small scale by Dr. Ure of Glasgow, and the manufacture has since been almost exclusively confined to that city, where it has assumed considerable importance. It was first made there in quantity in 1841, and the imports of kelp into the Clyde in that year amounted to 2565 tons. In 1845, there were four small works engaged in the manufacture of iodine. Kelp was then used for soap making on account of the sodium carbonate it contained, and the iodine was extracted from the lyes of the soapboilers. In 1846 there were twenty makers of iodine in Glasgow, who then treated the kelp directly, extracting also the potash salts which had a high value in the market. The fall in the price of potash salts owing to the discovery of the Stassfurt mineral, which reduced the price to one-third, the very variable character of the kelp used, and the extreme fluctuations in the price of iodine, ranging from 4*s.* to 34*s.* per lb., soon reduced the number of makers, and now there are only three works in Scotland. The produce of iodine from kelp was so limited that it offered unusual temptations to speculators, who derived most of the benefit from the high prices, the manufacturers suffering the losses during the low prices.

Moreover, the Scottish kelp industry, so far at least as the production of the kelp is concerned, has always been primitive and badly organised. Since 1905, however, there has been a marked increase in production, and under better conditions as regards organisation and methods the industry might well attain a state of prosperity (*cf.* Hendrick, The Value of Seaweeds as Raw Materials for Chemical Industry, J. Soc. Chem. Ind. 1916, 35, 13; also Scott, The Kelp Industry, Report to the Board of Agriculture for Scotland on Home Industries in the Highlands and Islands, 1914).

The history of kelp, or *varec* as it is called in France, is extremely interesting. It is a crude rough slag made by burning seaweed in long shallow pits. For many years it was a large and valuable article of commerce, and greatly enriched the proprietors of the West Highland estates where it was principally made. It was then the only source of soda. At the beginning of last century it realised 20*l.* to 22*l.* per ton, and the Hebrides alone yielded 20,000 tons per annum, worth upwards of 400,000*l.* It was largely used in soap making and in glass making, and within the last hundred years there were glass works at Dumbarton using this material, which were celebrated for the quality of their glass. At a glass works in Drontheim in Norway, it was still used for this purpose up to about forty years ago. The importation of barilla gave the first blow to kelp, and it fell in price, and for the twenty-two years ending 1822, the average price was 10*l.* 10*s.* The duty was then taken off barilla, and the price of kelp again fell to 8*l.* 10*s.*; in 1823, the salt duty was repealed and kelp fell again to 3*l.*, and in 1831 to 2*l.*, at which price there was no further profit on the manufacture. In the meantime soda was being largely made by the Leblanc process, and kelp was superseded altogether as a source of soda. It must have been a most expensive source, as it yielded only about 4 p.c. of alkali and often less than 1 p.c.; and at one time must have cost the soap makers what would have been equal to 100*l.* per ton for soda ash, worth now about 9*l.* 10*s.*

The manufacture of iodine and potash salts then began to assume some importance, but the kelp required was not the same, that which contained the most soda containing the least potash and iodine. Moreover the kelpers had been taught to burn at a high temperature, which improves the yield of sodium carbonate but volatilises much of the potash and some of the iodine. The seaweed employed by the kelpers was of a kind containing little iodine, and not very rich in potash. They used almost exclusively the black wrack, cut in large quantities in the Highland lochs, and consisting of the three fuci, *Fucus vesiculosus* (L.), *Ascophyllum nodosum* (Le Jol.), and *F. serratus* (L.), which are all uncovered at low tide. This is now entirely unutilised: the kelp made from it was known as *cut-weed kelp.* The average analysis from numerous cargoes of the kelp is shown top of next column

Potassium sulphate	23·08
Potassium chloride	1·45
Sodium chloride . . .	19·13
Sodium carbonate . . .	6·48
Insoluble	43·71
Water	6·22
	100·07
Total potash, K_2O . . .	13·40
Iodine, lbs. per ton . . .	4·18 =0·18 p.c.

Drift kelp is the only variety now employed as a source of iodine. It is made from the red wracks, the *Laminaria digitata* [(L.) Lamx.], or tangle, and the *L. stenophylla*, which are always submerged by the tide, and contain about ten times as much iodine as the fuci. These seaweeds are torn up by the storms from the rocks on which they grow, and cast ashore; unlike the black wrack, these plants suffer much from rain, the more valuable salts being completely washed away, and are often after drying quite valueless, the kelper losing all his labour. From the time of its discovery, the iodine was the most important product, but the potash salts were also very remunerative at first. Potassium chloride, or 'muriate,' as it is technically called, was worth 25*l.* per ton. The discovery of the Stassfurt mineral reduced its value to about one-third, and the further discovery of bromine in the same mineral reduced the price of that element from 38*s.* to 1*s.* 3*d.* per lb. The amount of bromine in kelp is small, only about one-tenth of the iodine, and it has not been extracted from this source for the last forty years. It is remarkable that the algæ should select iodine, as bromine is a much larger constituent of sea-water, which usually contains about 6 parts in 100,000, and according to Dittmar appears to bear the constant relation to the chlorine of 0·34 to 100, whereas iodine exists only as a minute trace, difficult even of detection, although the aggregate amount in the ocean must be enormous.

The algæ differ considerably in the proportion of iodine which they take up from the sea-water, and only two species, the *Laminaria digitata* and the *L. stenophylla*, are worth burning for kelp.

It is remarkable that the giant algæ of the Falkland Islands contain very little iodine, although these are the largest sea-plants in the world. The *Durillæa utilis* (Borg.), a marine tree with a stem a foot in diameter, and the *Macrocystis pyrifera* (Turn.) which grows to the length of 1500 feet, contain only traces of iodine; in some samples it can scarcely be detected.

The table (col. 1, p. 643) shows the average yield of the most important varieties. The kelp plant figures are taken from a large number of analyses, from seaweed gathered all around the shores of Great Britain and Ireland; also Denmark, Norway, and Iceland.

The seaweeds chiefly used in Japan for the extraction of iodine are *Laminaria sp.*, *Ecklonia cava*, *E. bicyclis* (Kjellm.), and *Sargassum sp.* The iodine content varies with the age of the algæ and also with the time of year, being greatest during June to September; the following figures give the iodine content of some of the raw seaweeds: *Ecklonia cava*, 0·23 p.c.; *E. bicyclis*, 0·27 p.c.; *Sargassum sp.*, 0·05 p.c.; *Laminaria angustata* (Kjellm.), 0·18 p.c.; *L. longissima*, 0·17 p.c.; *L. ocholensis*, 0·10 p.c.

According to Okuda and Eto (J. Coll. Agric. Tokyo, 1916, 5, 341), the greater part of the iodine in algæ is in organic combination. Of the total iodine found in *Ecklonia cava* 90 p.c

Dry weeds	Per cent.	lbs. per ton
Drift Kelp:		
Laminaria digitata [(L.) Lamx.], Tangle, stem	0·4535	10·158
,, *stenophylla*	0·4777	10·702
,, *saccharina* (Lamx.), Sugar Wrack	0·2794	6·258
Cut Kelp:		
Fucus serratus (L.), Black Wrack	0·0856	1·807
Ascophyllum nodosum (Le Jol.), Knobbed Wrack	0·0572	1·281
Fucus vesiculosus (L.), Bladder Wrack	0·0297	0·665
Various		
Halidrys siliquosa [(L.) Lyngb.], Sea Oak	0·2131	4·773
Japanese Seaweed, edible	0·3171	7·102
Himanthalia lorea [(L.) Lyngb.], Sea Laces	0·0892	1·998
Rhodymenia palmata [(L.) Grev.], Dulse, edible	0·0712	1·594
Chorda Filum [(L.) Stackh.], Sea Twine	0·1200	2·688
Zostera marina (L.), Grass Wrack	0·0157	1·023
Durvillæa utilis (Borg.), Falkland Islands	0·0075	0·179
Macrocystis pyrifera (Turn.), Falkland Islands	0·0308	0·690

was in a soluble organic form, and was not liberated by boiling with dilute sulphuric acid or potassium hydroxide. Fresh samples of *Ecklonia bicyclis* contained under 5 p.c. of the iodine as iodide, and 95 p.c. organic, of which 90 p.c. was soluble. The amount of iodine increases from winter to summer; old plants contain more than young plants. *Turbinaria fusiformis* (Yendo), *Sargassum enerve* (Ag.), and *Sargassum horneri* (Ag.) contained, respectively, 59, 78, and 66 p.c. of soluble organic, and 22, 16, and 17 p.c. of the soluble inorganic element. The Japanese food 'dashikombu,' made from *Laminaria* by partially fermenting and drying, contains 95 p.c. of its iodine in an inorganic state. Boiling with formalin, which converts the iodine into an inorganic form, is a test for the detection of organic iodine in algæ. The soluble iodine of *Ecklonia bicyclis* is precipitated by basic lead acetate, and by Stutzer's copper reagent, but the chief iodine compound in the aqueous extract is not combined with protein. Algæ from the open sea apparently contain more iodine than the same species from inland seas.

It will be seen that even in the drift weeds the quantity of iodine is inconsiderable, but if the plants are properly burnt to a loose ash at a low temperature, they ought to yield a kelp containing 25 to 30 lbs. of iodine to the ton. 12 lbs. per ton is, however, above the average yield from ordinary drift kelp. The kelpers often neglect to protect the seaweed from the action of rain, which washes out the soluble iodides, and moreover it is difficult to prevent them from burning it into a hard slag by working it up, when molten, with iron clauts. Sand and stones are thus mixed up with it, and the great heat employed drives off some of the iodine. The result is a hard slag of great density, and this density forms one of the difficulties in inducing the kelpers to burn the weed to a loose ash, which they imagine, from the lightness, will not give them the weight they expect. As an actual fact, of course, the total weight of the ash so produced is considerably more, from the same quantity of weed used; but old fallacies die hard, especially amongst the poor and ignorant people who do this work. There is the further disadvantage that the sulphates are reduced to sulphides or oxysulphides, and a considerable extra expenditure of oil of vitriol to decompose these is entailed; sulphur is thus obtained as one of the by-products of the lixiviation of kelp, in which it ought not to exist at all. The presence of silica as sand greatly assists the volatilisation of the iodine.

The following table shows the analyses of very good samples of Irish and Scotch kelp, and also of the latter burnt into loose ash, and the comparison of these indicates clearly the effect of the heat of burning:—

	Kelp		Ash
	Irish	Scotch	Scotch
Potassium sulphate	11·14	13·95	12·71
,, chloride	27·17	17·79	18·09
Sodium ,,	9·00	14·00	6·80
,, carbonate	5·82	3·92	3·43
,, sulphide	Heavy trace	Heavy trace	Slight trace
,, thiosulphate	1·22	0·75	0·17
,, iodide	0·82	0·76	1·48
,, thiocyanate	Heavy trace	Heavy trace	Slight trace
Soluble organic matter	Nil	Nil	0·42
Insoluble	41·41	44·80	49·75
Water	3·10	4·05	7·00
	99·68	100·02	99·85
Total potash, K_2O	23·17	18·77	18·32
Iodine, lbs. per ton	15½	14½	28
Carbon in insoluble part	Nil	Nil	9·00

A different method of manufacture was introduced by Stanford in 1863, when works were erected in the Outer Hebrides for the carbonisation of the stems of tangle (*L. digitata*) in closed retorts, thus converting the tangle into charcoal and collecting the products of destructive distillation, consisting principally of tar and ammoniacal liquor, in suitable condensers. A very porous charcoal is thus produced which contains all the iodine present in the seaweed employed; when lixiviated it gives very white salts containing no sulphides. The residual charcoal, after lixiviation, does not resemble that from wood, which is principally carbon with a small percentage of ash, but in its composition and general character approaches animal charcoal obtained from bone. The following table shows the comparison:—

	Seaweed	Bone
Carbon	52·54	11·77
Calcium phosphate	10·92	77·70
,, carbonate	15·56	1·43
,, sulphate	—	0·65
Magnesium carbonate	11·34	—
Alkaline salts	5·70	1·09
Silica, &c.	3·94	0·66
	100·00	100·00

The presence of magnesium carbonate is a peculiar characteristic of this charcoal, as all seaweeds are rich in magnesium salts. Seaweed charcoal, as might be expected from its composition, is an excellent decoloriser and deodoriser. As compared with animal charcoal it is much lighter and more bulky, and therefore has not replaced it as a decoloriser, although from its high percentage of carbon it would well stand the constant re-burning required in sugar works, and be improved by this treatment.

This process of carbonisation was in use in the islands of Tyree and North and South Uist for a number of years, with great benefit to the crofters and cottars of these islands. It required, however, the erection of separate carbonising works in each island, and, as the winter tangle only was used, it was difficult to secure sufficient supplies except from a large area. Moreover, it was found in practice very troublesome to completely extract the soluble iodides from the charcoal, and ultimately the process was abandoned in favour of the older and simpler method of kelp burning. A wet process of extracting iodine from seaweeds has also been tried. It had been noticed by Stanford that the whole of the alkaline salts present in the seaweed, and a considerable quantity of extractive matter containing dextrin and mannite, could be extracted from the fronds of the *Laminaria* or red seaweeds by simple maceration in cold water. The residue, which is the plant apparently unaltered, consists of a nitrogenous substance resembling albumen, to which the name of 'algin' has been given, and the algic cellulose or algulose, which represents the cellular fabric of the plant. The algin or alginic acid is removed by digestion with a solution of sodium carbonate, which dissolves it as sodium alginate, leaving the algulose. Dissolution can be effected in the cold, but it is necessary to employ heat, otherwise it is impossible to filter off the algulose. A Taylor filter is the only one that can be employed, the filtration being extremely difficult on account of the great viscosity of the algin or sodium alginate and the extreme fineness of the cellular algulose. The process adopted is to boil the seaweed with sodium carbonate, and filter; the algulose is separated by filtration, and the filtrate is mixed with hydrochloric acid, and the alginic acid is then easily filtered off; the solution is neutralised with caustic soda, evaporated to dryness, and carbonised, the residue forming the 'kelp substitute.' The alginic acid, which has a slight amber colour, is washed, bleached, and redissolved in sodium carbonate; the resulting liquor, evaporated in a vacuum pan, forms the commercial alginate of soda or 'soluble algin.' By evaporation on glass plates or porcelain slabs, the algin is obtained in the form of a transparent flexible sheet, which, however, tends to crack as it approaches dryness, and by immersing this in a very dilute solution of hydrochloric acid it is converted into alginic acid or 'insoluble algin,' which, without altering its appearance, renders the sheet perfectly insoluble in water. The soluble algin is a definite salt of sodium, having the composition, when pure, $C_{76}H_{75}O_{22}N_2Na_5$.

Commercial algin or sodium alginate resembles gum arabic, and in the sheet form can scarcely be distinguished from gelatin, from which it differs by the solution not gelatinising, and by giving no reaction with tannin. It is distinguished from albumen by not coagulating on heating; from starch by giving no colour with iodine; from dextrin and gum arabic by its insolubility in dilute acids. All mineral acids, and citric, tartaric, lactic, oxalic, and picric amongst the organic acids, precipitate alginic acid in a gelatinous form.

It precipitates all the alkaline earths as alginates, with the exception of magnesium, the alginate of which is soluble. It precipitates nearly all the heavy metals as alginates, but gives no precipitate with mercuric chloride, nor with potassium silicate. The following analyses show the usual composition of the commercial algin :—

	No. 1		No. 2		Average	
Water	17·13		19·30		18·22	
Organic matter	59·97		58·13		59·05	
Sodium carbonate	18·32	per cent. ash 22·90	17·78	per cent. ash 22·57	18·05	per cent. ash 22·73
Neutral salts	2·98		2·77		2·87	
Insoluble ash	1·60		2·02		1·81	
	100·00		100·00		100·00	
Soda, Na_2O	10·74		10·40		10·55	

This substance, known as soluble algin, is sodium alginate, but potassium, ammonium, lithium, or magnesium alginate are all soluble algins, and scarcely distinguishable in appearance. These all present the form of thin flexible sheets, resembling gelatin, and having the same colour, but none are gelatinous. The solution of algin resembles that of gum arabic, which in many of its applications it may be expected to replace; it is quite soluble in cold water, but the solution takes about 12 hours to complete. It is so extremely viscous that a 2 p.c. solution is as thick as a 50 p.c. solution of gum arabic, and a 5 p.c. solution is poured with difficulty out of a wide-mouthed bottle. Nearly all the mineral acids precipitate alginic acid ($C_{76}H_{80}O_{22}N_2$) from the solution as a very gelatinous precipitate; a 2 p.c. solution becomes semi-solid when thus treated. In this respect, it resembles a strong solution of egg albumen, and it can be employed for thickening colours in printing, or as a mordant in the same manner. Alginic acid is insoluble in water, so that in dressing fabrics the soluble algin forms a flexible varnish, which can be converted into a lustrous hard glaze by passing it through a weak mineral acid. This process, which would destroy the ordinary starch and gum dressings, renders it also permanent and insoluble in water, the fabric becoming waterproof. As the alginates of calcium, aluminium, iron, &c., are all insoluble, the same effect is obtained by the use of solutions of these metals for the final wash. Alginic acid when dry resembles albumen, but it can be obtained also in thin transparent sheets, and readily coloured like gelatin, from which, however, it differs in being insoluble in hot water. It can also be obtained in blocks. Calcium alginate ($C_{76}H_{74}O_{22}N_2Ca_3$) resembles it, but is whiter, like bone.

Aluminium alginate is very soluble in ammonia, and the aluminium ammonia alginate is insoluble when dry, so that it makes a cheap waterproof varnish. It forms a good mordant or dung substitute in dyeing. Copper alginate is soluble in ammonia, forming a beautiful blue copper ammonio-alginate, which is also insoluble when dry, and makes a varnish useful for waterproofing fabrics which are liable to decomposition or to attacks of insects.

Ferric alginate is also soluble in ammonia, forming a bright red ferro-ammonio-alginate: insoluble when dry, and proposed as a styptic, and for administering iron internally. These metals are most completely precipitated from solution by sodium alginate.

Nickel, cobalt, zinc, cadmium, manganese, chromium, uranium, silver, platinum, tin, arsenic, and antimony all form soluble ammonio-alginates, some of which are beautiful salts Sodium alginate, mixed with a dichromate, is sensitive to light in the same way as gelatin, the mixture becoming insoluble in water after exposure to light.

Alginic acid is a moderately strong acid, liberating carbon dioxide in the cold from the alkaline carbonates and from magnesium carbonate; in the latter case, the two insoluble substances in the presence of water form soluble magnesium alginate. The use of algin requires a thorough knowledge of its properties, on account of the numerous metallic salts which precipitate it, and with which it is therefore incompatible; these reactions limit to a great extent the application of the substance in solution as a substitute for gum and other bodies used for thickening purposes.

Algulose or algic cellulose contains no fibre, but consists of fine cellular tissue, which makes a transparent and very tough paper. It dries to a hard mass resembling ebony, but denser.

The kelp substitute in this wet process was obtained by evaporating and carbonising the acid liquor from which the alginic acid has been precipitated, after neutralising it with caustic soda. It should contain all the iodine and potash salts of the weed but no sulphides, and should yield about 30 lbs. of iodine to the ton. At the same time, in spite of the advantages which apparently would attend the adoption of this process, the manufacturing costs are so high and the demand for the products, other than iodine and potash salts, is so limited, that the process has not met with success on the commercial scale.

Lixiviation of kelp.—Little improvement has taken place in this process; the same simple method which has been in use for many years is still adopted in the Scotch works.

The kelp reaches the factory in large masses; these are first broken up into pieces about the size of road metal. The lixiviation is effected in rectangular iron vats with false bottoms; the vats are coupled together and heated by steam, and treated exhaustively. The whole arrangement is similar in every respect to that adopted in the lixiviation of black ash in the Leblanc process of soda manufacture. The solution is run off at about 40° at 45° Tw. This is evaporated in open hemispherical cast-iron boiling pans, about 9 feet in diameter, and the salts which deposit are fished out. In some works this boiling down is effected in cylindrical wrought-iron closed pans, heated by a coil of steam pipes round the inside of the pan, and provided with mechanical stirrers to keep the deposited salts in suspension. When the liquor is concentrated to 62° Tw., the whole is run out into a settler to allow the salts to deposit, and the supernatant liquor is run off hot into the crystallisers. In both cases the salt fished out or deposited is a crude potassium sulphate, which adheres a good deal to the pan and contains 50 to 60 p.c. of potassium sulphate, mixed with sodium sulphate and chloride The liquid is run into cylindrical iron coolers, and a crop of potassium chloride crystallises out in two or three days. The mother liquor is again boiled down, and the salt deposited is fished out; this salt is known as 'kelp salt,' and consists of sodium chloride, containing sodium carbonate equal to 8 to 10 p.c of alkali (Na_2O). The hot liquor is again run into the cooler, and another crop of potassium chloride is obtained. This process is repeated several times, kelp salt being fished out in the boiling pan, and potassium chloride crystallised out in the cooler. These successive crops of 'muriate,' as it is technically called, range in strength from 80 to 95 p.c. of potassium chloride.

The mother liquor is now rich in iodine, and is treated for its extraction. The several salts all contain iodine, and require careful washing to obtain it. These salts are known as 'Kelp salt,' which was formerly used for reducing the strength of soda ash, but is now unsaleable, 'Sulphate,' which is sold at a low price for manurial purposes, and 'Muriate,' which is largely used for the manufacture of saltpetre, potassium carbonate, chlorate, and dichromate, and the prussiates. The residual kelp waste formerly realised about 5s. per ton, and was employed in the common bottle glass manufacture; it consists principally of the carbonates of lime and magnesia, and some phosphates. It is all used as a manure in France, but in this country the farmers have always rejected it.

The following is the analysis of an average sample:

Salts of sodium and potassium	1·50
Carbon	3·09
Calcium sulphate	3·06
,, sulphide	1·70
,, carbonate	20·50
*Calcium and magnesium phosphates	6·72
Magnesium carbonate	6·89
Magnesia	2·22
Silicic acid and sand	20·82
Water	33·50
Total	100·00
*Containing phosphoric acid	2·70

The mother liquor, containing the iodides and bromides, also contains considerable quantities of sulphides, sulphites, and thiosulphates of sodium and potassium; it is mixed with about one-seventh of its volume of sulphuric acid, free from arsenic, about 145°Tw. (sp.gr. 1·725), and allowed to settle for 24 hours. This is effected in a closed lead-lined wooden vessel, provided with means to collect any sulphuretted hydrogen which may be given off. The sulphur compounds are decomposed, and a considerable deposit of sulphur takes place. This is known as 'Sulphur waste'; when dry it contains about 70 p.c. of sulphur, and is used in vitriol making. It also obstinately retains iodine, and long steaming is required to extract it. The liquor is strained off from the sulphur and run into the iodine still. This was formerly made of lead, but it now assumes the form of a deep hemispherical iron pot, heated by an open fire, and covered with a strong leaden lid, to which are luted two earthenware arms; these are connected with two series of stoneware udells, about ten in each set. These udells have stone stoppers beneath to allow any water containing chlorine, bromine, and iodine to drain off. The apparatus is shown in Fig. 1. Manganese dioxide is added at intervals to the contents of the still, and the iodine is carried over with the steam. The reaction is as follows:

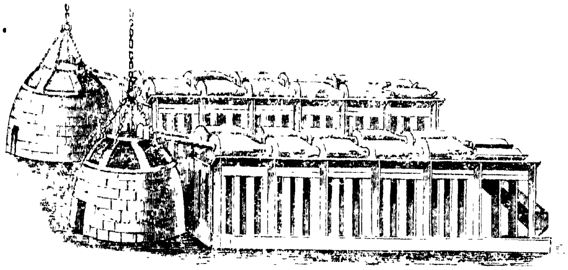


FIG. 1.

$$2NaI+3H_2SO_4+MnO_2$$
$$=I_2+2NaHSO_4+MnSO_4+2H_2O$$

Repeated distillations go on, without changing the udells, until these are full of iodine, the bulk of which, and the best, is found in the udells forming the centre of the series. The deposition of the iodine in successive layers squeezes much of the moisture out, and it is obtained in a firm, well crystallised form. The iodine on removal from the udells still contains moisture, and requires further treatment before the state of purity now demanded by consumers is attained. This old-fashioned process is the only one adopted in this country; many others have been proposed and tried, but have not been commercially successful. Commercial iodine is always sent out in 1 cwt. kegs; the consumption is usually reckoned in kegs, which means 1 cwt. It improves by keeping, becoming perfectly dry, and as it can be stored in a small compass, and often represents considerable value, it has been a favourite commodity for small speculative buyers. Bromine does not pay for the collection, but if it were required the arms would be changed and a simple worm-condensing arrangement of lead or earthenware, or a series of stoneware Woulff bottles attached: a further quantity of manganese dioxide would be added to the still, and the bromine distilled over. The liquor remaining in the still, and known as 'waste still liquor,' is a dense acid liquid of sp.gr. 1·235 to 1·500, containing sulphates of iron, manganese, potassium, and sodium; it is very troublesome to deal with and is run away as useless.

The following is the analysis of an ordinary average sample. One gallon contained 3·327 lbs. of dry salts:—

—	Liquor per cent	Dry salts per cent
Potassium sulphate .	5·13	15·42
Sodium sulphate .	9·10	27·36
Sodium chloride .	6·80	20·43
Manganous sulphate .	3·75	11·27
Ferric sulphate . .	3·00	9·02
Calcium sulphate .	0·19	0·57
Magnesium sulphate .	0·04	0·12
Sulphuric acid, free .	5·26	15·81
	33·27	100·00

The iodine used for medicine is resublimed in small earthen or porcelain covered pans, and is then known as 'resublimed iodine'; it is obtained in large brilliant plates, and is anhydrous. The pans employed must be shallow, as the vapour is very dense.

When iodine is badly made it may contain white needles, which consist of cyanogen iodide; it is now a rare impurity, but a very poisonous one.

In France a different method is adopted. After the precipitation of the sulphur in the mother liquor by addition of hydrochloric acid in slight excess, and boiling for some time, the clear liquor is drawn off and diluted with water to 40°Tw. Chlorine is then passed into the solution, until saturated, and the iodine is precipitated in a pulverulent form. Sometimes, instead of passing in chlorine, the calculated quantity of potassium chlorate is added to the solution; by interaction with the hydrochloric acid this salt yields the chlorine necessary for the liberation of the iodine. Great care must be taken that too much chlorine is not added, as iodine chloride may be formed, and go off as vapour. The clear liquor is then drawn off, and the iodine repeatedly washed by decantation to remove the salts. It is drained in earthen vessels with perforated bottoms, and finally dried on porous tiles. It is then resublimed. This is effected in ordinary earthenware retorts with short necks, and heated in a sand-bath in which they are completely immersed, the iodine being sublimed into earthen receivers. To recover the bromine from the liquor after extraction of the iodine, it is evaporated to dryness, and the residue is distilled in a leaden retort with sulphuric acid and manganese dioxide; it is collected in a receiver under strong sulphuric acid. The production of iodine in France has fallen off considerably; it is all used locally, either resublimed or made into potassium or other iodide, for which purpose the precipitated damp iodine suffices.

In Norway there are now nine or ten works engaged in the extraction of iodine from kelp. In Japan the chief kelp-producing districts are the province of Shima and the island of Hokkaido, but nearly all fishery districts yield a little. The industry is more or less scattered along the coast of Japan and is in the hands of many small producers, from whom the firms of iodine makers procure their supplies.

The Scottish seaweeds are considerably richer in iodine than the giant algæ of the Pacific and the Japanese seaweeds. In the United States the weed is collected at sea by a boat fitted with a power-driven cutting device which can be lowered to about 8 feet below the keel. From the boat the weed is delivered to an elevator, and carried to a closed drier, in which it is kept in constant motion at not above 100°. The dried weed is calcined at not above 400° in a brick kiln having a fire-clay lining, and a cast-iron grate through which air enters. The volatile products pass to condensers through a tar chamber, kept at a uniform temperature at the top, and superheated at the bottom. The ash is treated for the recovery of potassium salts, iodine, &c. (Board of Agriculture for Scotland Report, 1914, 118; *cf.* Turrentine, Met. & Eng. Chem. 1917, 16, 196; Higgins, *idem*, 1918, 19, 432).

Iodine from caliche. This mineral, the crude sodium nitrate of Peru and Chile, now forms by far the most important source of iodine. It contains iodine in the form of sodium iodate, which accumulates in the mother liquors from which the sodium nitrate has been crystallised. The proportion of iodine in the caliche varies considerably in the different deposits; in some it is absent altogether, in others it runs as high as 0·17 p.c. or 3·8 lbs. per ton; usually it does not exceed 0·02 p.c.

There are about 150 nitrate factories in Chile, but many of these are old and well worked out, and some are so badly situated as regards position and the raw material is of such a low grade, that they cannot work at a profit, and consequently are closed. At present about 100 factories are in operation, and their production of nitrate amounts to from 2,400,000 to 2,500,000 tons annually. Most of the factories are provided with plant for the extraction of iodine from the mother liquor, but, as their power of production of iodine is largely in excess of the world's power of consumption, the manufacturers have combined to restrict the output. The basis of the power of production of these factories is put down at 115,000 Spanish quintals (about 5100 tons) per annum, whilst the total quantity consumed is only a fraction of this amount. A certain percentage of the iodine sold in Chile year by year is allotted to each factory, and consequently there are rarely more than a few months in each year during which iodine is made, and there is always a very large stock in hand. The exports are naturally kept as nearly as possible equal to the requirements, but if any large increase in consumption took place there is no doubt that Chile could supply four or five times the quantity at present exported annually. The cost of recovering iodine as a by-product of the sodium nitrate industry is, in many cases, not more than from 1½*d.* to 2*d.* per oz.

It first came over in quantity in 1874, about 497 kegs. In the following year, 900 kegs were exported, and since then the export has continually increased. It was at first a very crude article, containing little over 50 p.c. of iodine, and a good deal was exported in the form of copper iodide. It is now, however, sent over in a pure state.

The following is the analysis of one of the samples of iodine sent from Peru in 1874:

Iodine	52·53
Sodium iodate	1·26
,, nitrate	11·62
Potassium nitrate	2·49
,, sulphate	1·78
Iodine chloride	3·34
Magnesium chloride	0·36
Insoluble matter	1·52
Water	25·20
	100·10

In 1877 the total production of iodine in Scotland was estimated at 1200 kegs; in France at 800 kegs. The present output does not reach these figures.

Japan began to export iodine in 1902, when 35 cwt. were sold. In 1904 the quantity exported was 612 cwt., in 1906 (consequent upon a fall in the price of iodine) only 196 cwt., and in 1907, 305 cwt.

In 1882, the export of iodine from Chile was 4116 cwt., in 1901 it had risen to 5280 cwt., and in 1912 it amounted to 7900 cwt., of a value of about 350,000*l.* This is about four times the present total production of the rest of the world.

The quantity of iodine sold throughout the world in 1887 was 6375 cwt., of which about 1000 cwt. were used in colour making. The present average annual consumption may be taken at nearly 10,000 cwt.

The final mother liquor, or 'aqua vieja,' from which the sodium nitrate has been crystallised, contains sodium iodate, nitrate, chloride, and sulphate, and magnesium sulphate. A good liquor contains about 0·3 p.c. of iodine.

It is run into wooden vats and the iodine is precipitated; the agent employed is sodium bisulphite in solution. The exact amount of iodine in the mother liquor is estimated, and a definite quantity of the solution is added to completely precipitate the iodine. As the bisulphite solution is run into the 'aqua vieja,' the liquid is stirred either by wooden paddle-wheels or by air forced up from perforated pipes at the bottom of the tanks. The latter method is quicker and more efficient, but the air carries away some of the iodine from the solution. The solution is then neutralised by addition of 'sal natron' liquor and again well stirred. After some time, most of the iodine settles to the bottom of the tank; any little that remains floating is removed by a calico bag at the end of a stick. The supernatant liquid is drawn off and used over again with the nitrate liquors.

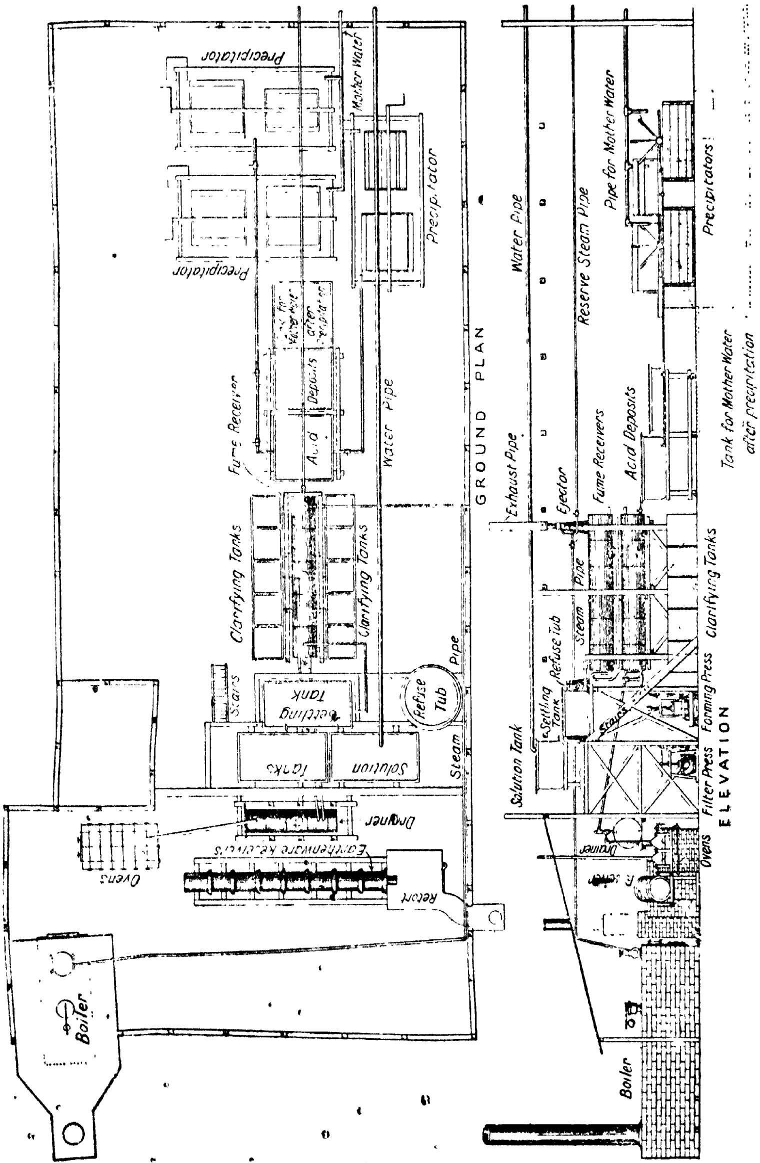
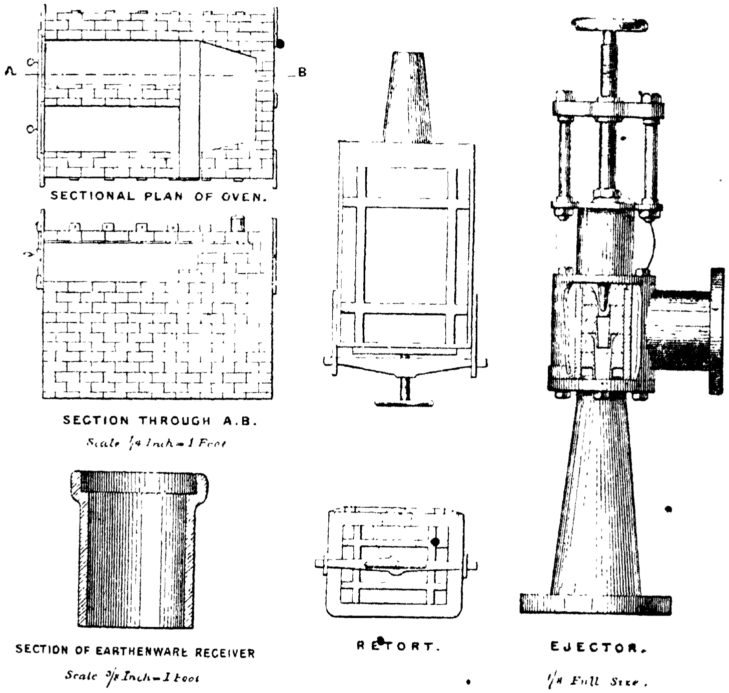


FIG. 2.

The iodine is washed with water, and pressed into thick cakes. It then contains 80 to 85 p.c. of iodine and 6 to 10 p.c. of mineral matter, and requires to be purified by resublimation. This is effected in a cast-iron retort, to which eight earthenware condensers or udells are attached in series. The retort is heated by a slow fire, and when the operation is completed the retort is allowed to cool, and the iodine removed from the udells. It is thus obtained pure. The complete plant is shown in the descriptive plans Figs. 2 and 3.

The sodium bisulphite is prepared by passing the fumes of burning native sulphur into a solution of 'sal natron' or sodium carbonate. The sulphur, which is one of the many minerals found in this interesting region, is burned on an iron plate in a plain iron oven, and the fumes drawn by a steam injector into perforated pipes in the solution of sal natron. The manufacture of this substance is also peculiar to the district. It is obtained by burning together 85 parts of crude sodium nitrate, obtained from the 'aqua vieja' tanks, and 15 parts of coal. The mixture is made in the form of a cone 5 feet high, with a space of 2 feet dug out round the base. It is saturated with water and ignited; the sodium carbonate thus formed fuses and runs out into the pit. It is dissolved in water, and the solution is pure enough for use in this process, the impurities consisting of sodium sulphate and chloride, the unburnt coal being left in the residue undissolved.



SECTIONAL PLAN OF OVEN.

SECTION THROUGH A.B.

Scale 1/4 Inch = 1 Foot

SECTION OF EARTHENWARE RECEIVER

Scale 3/8 Inch = 1 Foot

RETORT.

EJECTOR.

1/8 Full Size.

FIG. 3.

Uses of iodine.—About one-fifth of the total consumption of iodine is employed in the manufacture of aniline colours; a good deal of this is recovered and used again. It is principally used in the manufacture of Hofmann violet, and aniline green in the form of methyl iodide; also for making erythrosin and the blue shade eosins, in which iodine is made to react upon fluorescein. Some substitution products are occasionally made, such as the ethylated chrysaniline. A small quantity is used in photography, but the bulk of the iodine of commerce is employed in medicine. Iodine, iodoform, and the iodides of arsenic, iron, lead, mercury (red iodide), potassium, sodium, and sulphur are all official in the British Pharmacopœia; the preparations employed will be referred to under their respective names. Hydriodic acid, ethyl iodide, and iodides of ammonium, cadmium, mercury (green iodide), and starch are also used in medicine, and each will therefore be noticed. Iodine, if pure, should sublime without residue, and the portion subliming first should not include any slender colourless prisms emitting a pungent odour (cyanogen iodide). A solution in chloroform should be perfectly clear, denoting absence of moisture. The British Pharmacopœia directs that 0·5 gram dissolved in 50 millilitres of water, containing 1 gram of potassium iodide, should require for complete decoloration at least 39 millilitres of the $N/10$-solution of sodium thiosulphate.

It is employed in the B. P. in the form of

Tinctura iodi fortis and *Tinctura iodi mitis*, and *Unguentum iodi*. In the tincture it is dissolved with potassium iodide in rectified spirit and water. In the ointment the same ingredients are employed, substituting lard and glycerin for the spirit.

A volumetric solution of iodine dissolved in potassium iodide is used in the laboratory for titrating solutions of arsenious acid, sulphurous acid, and sodium thiosulphate. It contains 12·7 grams of iodine in 1000 c.c., and corresponds to 1·7 gram of sulphuretted hydrogen, 3·2 grams of sulphur dioxide, and 4·95 grams of arsenious oxide. Iodine is also used for testing oils, which differ as to the amount absorbed, and some can be distinguished from others by this means (*v.* OILS, FIXED, AND FATS).

Other unofficial preparations of iodine are also employed in medicine. *Glycerinum iodi* is iodine dissolved in glycerol, used for external application. *Pigmentum iodi*, Coster's paste, is iodine dissolved in light oil of wood tar, and used for ringworm. *Tinctura iodi decolorata* is a tincture made with rectified spirit, and in which the iodine is decolorised by ammonia. It is used for chilblains. *Collodium iodi* is flexible collodion containing 30 grains of iodine to the ounce, and is very useful for painting on wounds. Carbolised iodine solution is a colourless mixture of tincture of iodine, phenol, and glycerol in hot water; it is used as a gargle or pigment in diphtheria, and internally for Asiatic cholera.

Medicinal properties of iodine.—Iodine was first employed in medicine in the form of burnt sponge, a remedy long used in treating goître. When administered internally it is usually in combination with an alkali; taken alone it is an irritant poison. It is a most powerful alterative, impoverishing the blood and stimulating the absorbents. It is antisyphilitic and antiscrofulic. In syphilis, scrofula, and chronic rheumatism it is largely used, and especially in swellings of the joints and enlarged glands, which are also treated by painting externally with tincture of iodine, in which it acts as a counter-irritant. It has a remarkable power in expelling both mercury and lead from the system. The vapour mixed with steam from hot water is useful in inhalation for many affections of the air passages. Long-continued use may give rise to the depressing nervous train of symptoms known as iodism, and for which belladonna is employed as an antidote. Copious drinks of solution of starch form the antidote in cases of poisoning. Used alone, iodine is a powerful disinfectant and decoloriser, acting in the same way as chlorine. It may be allowed to evaporate spontaneously, but is very apt to colour the sheets, blinds, or anything dressed with starch; it is also used in candles, the burning of which volatilises it.

Hydrogen iodide HI is a colourless gas, very soluble in water and resembling hydrogen chloride; it forms dense white fumes in the air; its sp.gr. is 4·3737. Mixed with dry oxygen and exposed to bright sunshine, it is rapidly decomposed with liberation of iodine. It liquefies under pressure, b.p. −35·5°; m.p. −50·9°; latent heat of vaporisation, $21{\cdot}6 \times 10^{10}$ ergs. It is composed of equal volumes of iodine and hydrogen, and contains 99·2 p.c. of its weight of iodine. The aqueous solution is colourless, but on exposure to air it becomes coloured by the deposition of iodine from oxidation. It is decomposed by sulphuric and nitric acids, and by chlorine and bromine, which set the iodine free. By passing the gas into ice-cold water a solution may be obtained of sp.gr. 1·99.

The following table shows the relative percentage of hydriodic acid at different specific gravities:—

Sp gr. at 15°	Per cent. of acid
1·708	51·9
1·551	47·2
1·442	39·2
1·297	30·3
1·175	18·5
1·083	5·9

It is usually prepared in solution by passing sulphuretted hydrogen into water in the presence of iodine: $H_2S+I=2HI+S$. At first the action is slow on account of the deposition of sulphur covering up the iodine and preventing its solution; the hydriodic acid when formed, however, dissolves an increasing proportion of iodine, and by the gradual addition of iodine and water as the action progresses, large quantities of hydriodic acid may thus be obtained up to a sp.gr. of 1·56.

A modification of this process for very pure acid has been proposed by Winkler. The iodine is dissolved in carbon disulphide, and the solution covered with a stratum of water; when the sulphuretted hydrogen passes into the mixture, the hydriodic acid dissolves in the water, and the sulphur in the carbon disulphide. The aqueous solution only requires boiling for a few minutes to expel the sulphuretted hydrogen, and to obtain the hydriodic acid quite pure.

Another method was suggested by Kolbe. One part of amorphous phosphorus is added to 15 parts of water in a tubulated retort filled with carbon dioxide, and 20 parts of iodine gradually added. The resulting liquid is allowed to stand and then heated for a short time, cooled, mixed with 4 parts of water and distilled. It yields a colourless acid free from uncombined iodine: $P+5I+4H_2O=5HI+H_3PO_4$. It may also be obtained by heating potassium iodide with a syrupy solution of phosphoric acid. Hydriodic acid is employed in the manufacture of some of the iodides, and is used in medicine in the form of syrup.

Iodic acid HIO_3. This acid is usually prepared by boiling iodine in strong nitric acid, free from nitrous acid. It is, however, best obtained by the oxidation of iodine by chloric acid in about 25 p.c. strength:

$$I_2+2HClO_3=2HIO_3+Cl_2$$

Iodic acid is deposited in crystals of sp.gr. 4·487. When heated it gives off water, and iodine pentoxide I_2O_5 is obtained in small white crystals. It is very soluble in water, and easily decomposed by reducing agents forming hydriodic acid and free iodine. For reduction of iodic acid solutions with sulphurous acid, *see* Landolt, Ber. 1886, 19, 1340; 1887, 20, 745; Patterson and Forsyth, Chem. Soc. Trans. 1912, 101, 40.

The normal iodates have the general formula MIO_3. Acid iodates are also known.

Potassium iodate KIO_3 forms small white cubic crystals. It may be obtained by carefully heating a mixture of 2 mols. potassium chlorate and 1 mol. iodine $2KClO_3+I_2=2KIO_3+Cl_2$, or by the electrolysis of potassium iodide in presence of potassium chromate. Sodium iodate $NaIO_3$ crystallises in small eight-sided prisms. Both salts are poisonous. Both are obtained in considerable quantity in the manufacture of the respective iodides by No. 2 process as described below. The iodates can easily be separated by taking out the first salts deposited on evaporation, as these are less soluble than the iodides. If iodic acid were required on the large scale, it could be easily made as a by-product of the iodide manufacture by crystallising out the iodate before fusion, and precipitating it with barium chloride as barium iodate. This is then decomposed by sulphuric acid.

Iodine iodate $I(IO_3)$ may be prepared by the action of ozone on iodine, or by warming iodic acid with concentrated phosphoric acid (D 1·70). Oxygen and then iodine are evolved and a yellowish-white precipitate formed.

Periodic acid is known only in the form of a hydrate $HIO_4,2H_2O,(H_5IO_6)$. It is a colourless crystalline deliquescent solid, m.p. 133°. On heating it is completely decomposed into iodine pentoxide, water, and oxygen. It may be obtained by electrolysing an aqueous solution of iodic acid contained in a porous cell immersed in dilute sulphuric acid, the lead anode coated with lead peroxide being placed in the iodic acid solution and a platinum cathode in the sulphuric acid. The various periodates may be grouped as derived from *metaperiodic acid*, HIO_4; *diperiodic acid*, $H_4I_2O_9$; *mesoperiodic acid*, H_3IO_5; and *paraperiodic acid*, H_5IO_6.

Iodine trichloride ICl_3 is obtained in orange-yellow crystals by passing chlorine into a flask containing iodine vapour sublimed from a small retort. It is a very active disinfectant and germicide in solution of 1 to 1000. It has been used in medicine internally. In contact with organic matter, chlorine and iodine are liberated in a nascent state.

Iodine perchlorate $I(ClO_4)_3 2H_2O$, greenish-yellow needles, formed by dissolving iodine in anhydrous perchloric acid, cooled by ice and salt, and oxidising with ozone. The water is due to the reaction with ozone:

$$I_2+6HClO_4+O_3=2I(ClO_4)_3+3H_2O$$

Cyanogen iodide CNI. This very poisonous substance is interesting as forming an occasional impurity in commercial iodine; it is very seldom met with now, and ought never to be present if the manufacture is properly carried out. Its occurrence is probably due to an insufficient addition of oil of vitriol to the saturating vat or to the iodine still. It is usually prepared in the laboratory by the distillation of iodine with mercuric cyanide, or by dissolving iodine in concentrated solution of potassium cyanide. It presents the appearance of exceedingly fine silky needles, colourless, and very volatile, even at ordinary temperatures, and with a penetrating pungent odour which excites tears. It sublimes without change. It is sparingly soluble in water, easily so in alcohol, and in ether, and also in fixed and volatile oils. The aqueous solution does not give the starch reaction of iodine, nor does it precipitate silver nitrate.

Sulphur iodide S_2I_2 is a dark crystalline substance, obtained by gently heating in a glass flask 1 part of sulphur with 4 parts of iodine until the mixture liquefies; the flask is then broken, and the crystalline mass removed. It appears to be a solid solution of sulphur and iodine. It is insoluble in water, but soluble in glycerol. It has the odour and staining properties of iodine. It is occasionally used in medicine externally in skin diseases applied in an ointment.

Arsenic tri-iodide AsI_3. This substance forms small orange-coloured crystals, soluble in water and in alcohol; it has a neutral reaction, and gives a yellow precipitate with sulphuretted hydrogen. Heated in a test-tube it almost entirely volatilises, violet vapours of iodine being set free.

It is prepared by direct combination of metallic arsenic and iodine, or by evaporating together to dryness solutions of arsenious and hydriodic acids. The Pharmacopœia preparation is *Liquor arsenii et hydrargyri iodidi*, 1 gram of each ingredient in 100 millilitres, and the dose is 3–12 decimils.

Nitrogen iodide $N_2H_3I_3$ or $NH_3{\cdot}NI_3$ is a dark brown powder, obtained by adding iodine to excess of solution of ammonia, or by the action of ammonia on iodine chloride containing free hydrochloric acid. It is a most violent explosive, but its action is uncontrollable, and it is impossible to keep it in safety. It has therefore found no commercial application, but has been proposed as a chemical photometer on account of the ease with which it is decomposed by light in presence of excess of ammonia (*v.* Guyard, Ann. Chim. [vi.] 1, 368).

Iodo-azoimide N_3I is formed by the action of an ethereal solution of iodine on silver azoimide at 0°. It is a white solid and very explosive, forming nitrogen and iodine.

Ammonium iodide NH_4I. This is a white crystalline salt, very deliquescent and becoming yellow on exposure to air. It is prepared by saturating hydriodic acid with ammonia, by shaking powdered iodine with hydrogen peroxide solution and gradually adding ammonia solution, or by decomposing iodide of iron with ammonium carbonate and filtering off the iron precipitate. The solution in each case is evaporated and set aside to crystallise. It is used in photography, and also in medicine instead of potassium iodide, especially in rheumatism, as causing less depression than the potassium salt. It must be kept from the access of light and air, as iodine is freely given off. It is soluble in alcohol.

Bromine acts upon it with formation of *ammonium bromoiodobromide* $NH_4{\cdot}BrIBr$, crystallising in large ruby-red prisms, green by reflected light. Similar compounds are formed by the iodides of potassium, cæsium, and rubidium, but not with sodium.

Potassium iodide KI. This is the most important of the iodides, and forms a considerable article of manufacture, as the greater portion of the iodine of commerce goes into consumption in this form. It is a colourless and odourless salt crystallising in large cubes.

and permanent in the air. It contains no water of crystallisation, and is very soluble in water, dissolving in two-thirds of its weight. It is also soluble in alcohol. There are three methods employed in the manufacture.

1st. Hydriodic acid is saturated with potassium carbonate, and the solution evaporated and crystallised. This is the most direct method, and there is no loss; it gives a pure product, but it is expensive and tedious.

2nd. Iodine is dissolved in solution of caustic potash. This produces a mixture of potassium iodide and potassium iodate; the reaction is $3I_2 + 6KOH = 5KI + KIO_3 + 3H_2O$. The solution is evaporated to dryness, a little charcoal is added, and the product fused in an iron pot at a red heat until all the iodate is decomposed, and potassium iodide alone remains. The mass is dissolved in water, the solution filtered and crystallised.

3rd. Iodide of iron is first prepared by the addition of iron borings and iodine to water; the latter must be added gradually to keep down the temperature; the solution is filtered, mixed with potassium carbonate and the iron precipitate washed and filter-pressed. The solution is then evaporated to dryness and the residue redissolved and crystallised.

This process is that most commonly adopted by manufacturers. The crystallisation is performed in enamelled iron pans, surrounded by a steam jacket in brickwork, and very gradually cooled. The best crystals are obtained on fluted glass rods suspended in the liquid.

Potassium iodide is used in photography, but medicine is the principal outlet, and requires a large consumption. It is a powerful alterative, diuretic, and absorbent; and is much administered internally, especially in rheumatism and syphilis. Its properties are similar to those of iodine. As iodine is freely soluble in potassium iodide solution, it presents an excellent form for its internal administration.

It must contain no iodate; this is easily detected by the addition of tartaric acid and starch solution, which sets free hydriodic acid, and if there be any trace of iodate present, free iodine is liberated, as shown by the blue colour of the iodide of starch. Potassium iodide should not contain water, and therefore should not lose weight when heated; it should contain no sulphate, and therefore give no precipitate with barium chloride insoluble in nitric acid. A feeble alkaline reaction from the presence of a slight trace of carbonate, indicated by cloudiness with lime or baryta water, soluble in nitric acid, is allowed by the London Pharmacopœia (but not by the German) as tending to retain the colour of the iodide when long kept. Chlorides of potassium or sodium are a common impurity; the presence of a chloride is shown by precipitating with silver nitrate, and agitating the precipitate with ammonia. The ammonia solution should give no precipitate with nitric acid. 0·5 gram should require for complete precipitation not less than 29·8 or more than 30·5 millilitres of $N/10$-solution of silver nitrate. It is almost impossible to obtain this salt, when made on the large scale, quite free from chloride (the B.P. allows a 'very little') as potassium carbonate cannot be prepared in quantity without it; a good iodide contains:

Potassium iodide	99·4
,, chloride	0·2
Water	0·4
	100·0

This salt is officinal in the following preparations. *Linimentum potassii iodidi cum Sapone*, *Liquor iodi*, *Tinctura iodii*, *Unguentum iodi*. Potassium iodide is sometimes administered in large doses, and it is important medicinally that it should contain no iodate, as this salt is poisonous; it must not be prescribed in mixtures containing potassium chlorate, for this salt decomposes it, forming iodate.

Sodium iodide NaI. This salt is obtained as a deliquescent white crystalline powder, soluble in two-thirds of its weight of water. It may be prepared by the same methods as the corresponding potassium salt; that from ferrous iodide is usually employed, and the solution is simply evaporated to dryness. It crystallises in anhydrous cubes and also in hexagonal plates, having the formula $NaI,2H_2O$. It is used in medicine for the same purposes as potassium iodide, but the principal application is as a precipitant of silver and gold from the weak copper ores of the Tharsis and other copper-extracting companies. The same tests as with the potassium salt may be used for its purity; 1 gram requires 66 c.c. of the volumetric solution of silver nitrate for complete precipitation.

All the alkali iodides when dry absorb bromine and chlorine forming additive compounds of the type MIX_2 and MIX_4, where X is the added halogen, *see* Wells and Wheeler (Amer. J. Sci. 1892, [iii.] 44, 42; Filhol, J. Pharm. Chim. 1839, 25, 435, 506; Rae, Chem. Soc. Trans. 1915, 107, 1286; 1918, 113, 880).

Ferrous iodide FeI_2 is a crystalline green deliquescent mass. It is employed in medicine in the form of syrup of iodide of iron, in which it can be better preserved. It is a tonic alterative useful in anæmia of scrofulous patients, especially children.

A similar syrup of manganese iodide is also sometimes used in medicine.

Zinc iodide ZnI_2. An easily fusible compound which sublimes in needles. It is prepared in the same way as the iron salt, and obtained by evaporation as a white crystalline deliquescent salt. It is sometimes used in photography.

Lead iodide, or *Plumbic iodide*, PbI_2, is a brilliant yellow powder, made by precipitating a solution of lead nitrate with potassium iodide, and washing and drying the precipitate. By boiling the powder in water, and allowing the solution to cool, it is obtained in bright yellow crystalline scales. It is employed in medicine externally in the form of ointment.

Mercurous iodide HgI, or *Green iodide of mercury*, is a green insoluble powder, which darkens on exposure to light. It is prepared by rubbing together in a porcelain mortar the equivalent proportions of mercury and iodine, and moistening the mixture with alcohol until the metallic globules cease to appear and a green powder is obtained. This must be dried in the air in a dark room, and preserved in a bottle put away from the light. It can be obtained in yellow crystals by sublimation. It is insoluble in water and alcohol (*v.* MERCURY, COMPOUNDS OF).

Mercuric iodide, or *Red iodide of mercury,* HgI_2. This is a brilliant scarlet powder, known as Chinese vermilion. It may be prepared in the same manner as the green iodide, using double the equivalent of iodine; but a better product is obtained by precipitation. A solution of mercuric chloride, or corrosive sublimate, is precipitated with potassium iodide, both salts being dissolved in boiling water; the precipitate is washed and dried over the water-bath. By sublimation it may be obtained in large and beautiful crystals, which when hot are yellow, but reassume their scarlet colour on cooling. It is insoluble in water, but very soluble in solution of potassium iodide. This solution contains a double iodide of mercury and potassium and is used in analysis as a precipitant for alkaloids. It forms a pigment more brilliant than vermilion, but it is not much used for this purpose, as it is easily altered by exposure. It is employed in medicine, especially in syphilis, in doses of a thirty-second to an eighth of a grain, and also externally as an ointment. The official preparations are *Liquor arsenii et hydrargyri iodidi* and *Unguentum hydrargyri iodidi rubri*. It has been used as a germicide for washing wounds, instead of corrosive sublimate, which is not so effective and is more poisonous. It has also been used as an antifermentive in tanning (*cf.* MERCURY, COMPOUNDS OF).

Bismuth iodide BiI_3 is a red powder obtained by precipitation from bismuth nitrate by potassium iodide. It has been introduced into medicine as a substitute for iodoform in treating wounds. It has no odour. This iodide is soluble in potassium iodide, forming a double iodide employed in analysis as a precipitant for alkaloids.

Silver iodide AgI. This salt occurs native, in hexagonal crystals, as *iodargyrite* or *iodyrite*. It is obtained by precipitation from a solution of silver nitrate and any soluble iodide. This salt is not employed commercially in this form. It is the active salt of iodine which is used in photography. It is the form in which iodine is often precipitated and weighed. It is almost insoluble in ammonia, but soluble in potassium iodide and cyanide, and in sodium thiosulphate.

Palladium iodide PdI_2. This is a dark-brown powder, interesting as a form in which palladium is estimated in analysis.

Cuprous iodide Cu_2I_2. When solutions of potassium iodide and cupric sulphate are mixed, only half the iodine is precipitated as cuprous iodide, the other half being set free, according to the following equation:

$$2CuSO_4+4KI=Cu_2I_2+I_2+2K_2SO_4$$

It is necessary, therefore, to add a reducing agent as sulphurous acid or sodium thiosulphate, but ferrous sulphate is usually employed; the whole of the iodine is then thrown down as cuprous iodide

$$2CuSO_4+2FeSO_4+2KI =Cu_2I_2+K_2SO_4+Fe_2(SO_4)_3$$

The former reaction was proposed by Soubeiran as a method of obtaining iodine from kelp liquors, but it has not been much used.

Cuprous iodide is a white crystalline solid, insoluble in water; on exposure to a red heat it fuses to a brown mass. The iodine can be separated from it by heating it with manganese dioxide or strong sulphuric acid. Or it may be decomposed by boiling with water and zinc, which yields zinc iodide and metallic copper. Or it may be treated with potassium or sodium hydroxides or carbonates, which decompose it, forming cuprous oxide and potassium or sodium iodide. With ammonia it combines, forming ammonio-cuprous iodide $CuI.2NH_3$: a white crystalline powder.

Iodide of starch, or *Iodised starch*, is a dark blue powder obtained by triturating iodine with a little water and adding gradually starch in powder until it assumes a deep and uniform colour, and drying at a low temperature. It is decolorised at 100°. It has been used in medicine as a mild form of administering iodine internally, and in the form of a paste to cleanse and heal foul sores and ulcers.

Estimation of iodine.—The violet vapour of free iodine is characteristic, and there are also four very sensitive tests for iodine and iodides: for the former the blue colour test with starch, and the crimson solution in chloroform, benzene, or carbon disulphide; for the latter the precipitation as silver or palladium iodide. All these can be employed in estimating iodine, the colour tests by comparison with standard solutions, and the gravimetric tests by weighing the iodine as silver iodide or palladium iodide. Insoluble iodides must be converted into alkaline iodides before precipitation by silver nitrate or palladium chloride. This may be effected by fusing with sodium carbonate, or preferably by a mixture of this and potassium carbonate. Another method for a metallic iodide is to suspend it in water and pass sulphuretted hydrogen through the mixture; the metal is precipitated as a sulphide, and hydriodic acid formed. Silver iodide is generally heated with zinc and dilute sulphuric acid, the silver is reduced to the metallic state, and zinc iodide remains in solution.

If the iodine exists in the form of a soluble iodate it must be reduced to an iodide by sulphurous acid. With organic iodides it is usual to ignite with pure sodium hydroxide.

In the colour tests, the iodine must be set free by bromine, chlorine, or, preferably, nitrosulphuric acid. The starch method, owing to the easy decomposition of the iodide of starch, is not generally available, but the separation of the iodine from solution by a solvent forms a process of great accuracy, of easy and rapid execution, and of general application. In estimating the iodine in kelp or seaweed ash, or kelp substitute, the following process is adopted. Kelp is not an easy cargo to sample. There is often great difference in the value of the large masses forming the cargo. Stones and sand are a frequent cause of annoyance; stones are often found fused into the centre of a block of kelp, and forming most of the block. These can only be detected by breaking up all the large pieces. With seaweed ash, or charcoal, or kelp substitute there is no difficulty. Where there is much sand the kelp is more friable. The sand is generally composed of shells, and is mostly carbonate of lime; but it is sometimes quartz, flint, or other forms of silica. To ensure an accurate sample, about 100 lbs. are carefully picked from a cargo of, say, 100 tons, and ground up. A portion of this is finely powdered and kept as a sample for reference. Of this, 5 grams are taken to estimate the moisture, another 5 grams are taken to estimate the soluble matter, the carbon, and the ash, also the potash and the iodine in the soluble matter. The kelp is treated with about 75 c.c. of hot water, which dissolves little or none of the oxysulphides. This operation is repeated and the residue washed, and the solution made up to 250 c.c. In a portion of this the potash is estimated by platinum tetrachloride. For estimating the iodine, one-tenth part or 25 c.c., equal to 0·5 gram of kelp, is taken. This will not contain more than 5 milligrams of iodine, generally about 2 milligrams, often only 0·5 milligram. If the amount exceeds 5 milligrams, it is advisable to dilute the solution with an equal bulk of water. Five c.c. of carbon disulphide are then added and a few drops (one to three) of nitro-sulphuric acid dropped in. This reagent is prepared by treating starch with nitric acid, and passing the nitrous fumes into sulphuric acid of 1·843 sp. gr. to saturation. The mixture keeps perfectly well. The testings are performed in large even test-tubes, and compared with graduated standard solutions of potassium iodide treated in precisely the same manner. By this method $\frac{1}{250000}$th part of iodine is easily detected and measured, and up to $\frac{1}{1000000}$th part the estimation is very accurate. It has several advantages over the use of starch, as besides the introduction of an organic substance liable to change, the blue colour of the iodide of starch is distributed over the whole liquid, and when dilute can only be seen by looking down the length of the tube. Moreover, the solution is not transparent, and the indications are not sharp enough for accurate quantitative work, though useful often in testing. The carbon disulphide method is quite as sensitive, and the iodine is removed from the solution and concentrated in a sixth of the volume at the bottom of the tube. The maximum effect, which takes time with the starch, is immediate in this case. The carbon disulphide solution of iodine can be removed, and the iodine recovered from it by an alkali for further experiment if desired, but it is quite unnecessary for accurate results. It is usual to remove it from the disulphide by zinc in the presence of water, so that the reagent can be used over and over again. Many years of experience of this and other processes have shown that this is the only one to be relied on where many such estimations have to be performed daily, especially in kelp and its products, which contain such a small proportion of iodine. If the iodine is to be determined in a seaweed or other organic material, the sample must always be carbonised in a small iron retort or close crucible, and not burnt to ash in an open crucible. The salts are washed out from the charcoal, and the carbon and ash estimated by burning the residue. If this be not done, it is almost impossible to completely burn away the carbon in the presence of so much alkaline salts which at a high temperature fuse and cover it over. If, moreover, a long time is taken, as it must be, over an ordinary Bunsen burner, a large portion of the potash and all the iodine may be easily burnt off. If the salts contain magnesium, as all those from seaweeds do, it is necessary to make sure that there is an excess of alkali present, or the iodine will be rapidly burnt off. In kelp and seaweed there always is sufficient alkali, and this precaution is unnecessary, but where the object is to estimate iodine in organic substances containing it in minute traces, more caustic soda should always be added before carbonising. As all seaweeds also contain soluble sulphates which become reduced to sulphides and oxysulphides when burnt to ash, carbonisation presents another advantage, as it prevents this change.

Palladium chloride is the only reagent which can be relied on for the direct gravimetric estimation of iodine in mixed liquors containing chlorides and bromides. The kelp liquor must be mixed with hydrochloric acid and set aside in a warm place till the sulphur compounds are decomposed, it is then filtered off and precipitated with palladium chloride, and allowed to stand for some time. The black precipitate of palladium iodide may be washed with hot water, and lastly with a little alcohol, dried at a gentle heat, and weighed on a tared filter; 100 parts contain 70·45 parts of iodine. Or it may be ignited in a platinum crucible, and the iodine calculated from the weight of the palladium left; 100 parts of palladium are equal to 237·9 parts of iodine. If chlorine is also to be estimated in the same liquid, palladium nitrate must be substituted for the chloride. If bromine is also present the chloride must be used, or a soluble chloride must be added, or the bromine will be precipitated with the palladium iodide. This method gives discordant results with kelp, on account of the cyanides often present. Free alkalis, chlorine, and bromine also prevent the precipitation.

In 'caliche' the iodine exists as an iodate, and this must be first reduced to an iodide by sulphurous acid or sodium bisulphite. There are several methods of estimating iodine, bromine, and chlorine, directly and indirectly, when present together. A very simple method of separating these elements directly is to distil over the iodine first by boiling with ferric sulphate; it may be condensed in solution of potassium iodide and titrated with sodium thiosulphate. The bromine is then separated from the residue in the retort, which has been allowed to cool, by gently warming the solution after addition of potassium permanganate, and distilling it into solution of ammonia in excess, in which it is titrated with an acid; or estimated gravimetrically by precipitation as silver bromide. The chlorine can be estimated in the residue or by difference from a determination of the total quantity of chlorine, bromine, and iodine in the original substance by precipitation as silver salts. Another method is to distil over the iodine with a concentrated solution of potassium dichromate; after the iodine is removed the addition of a little sulphuric acid to the retort will set free the bromine, the chlorine can then be determined as in the last process.

Field's method of separating these three halogens is to divide a solution into three equal parts; each portion is precipitated by silver nitrate. No. 1 is washed, dried, and weighed. No. 2 is digested with potassium bromide, then washed, dried, and weighed. No. 3 is digested with potassium iodide, then washed, dried, and weighed. No. 1 contains the silver chloride, bromide, and iodide. No. 2 contains only silver bromide and iodide, the chloride having been by this process converted into bromide. No. 3 contains silver iodide only, the chloride and bromide having been both converted into iodide. The exact quantities of each in the solution can therefore be easily calculated. The valuation of commercial iodine has been alluded to already; the sodium thiosulphate is usually standardised by titrating it with a potassium iodide solution of pure iodine. 100 c.c. = 2·48 grams ($\frac{1}{100}$th of $Na_2S_2O_3,5H_2O$) and is equal to 1·27 grams of iodine ($\frac{1}{100}$th of atomic weight in grams). Another method of volumetrically estimating the strength of an iodine solution is to pass sulphuretted hydrogen into it until decolorised; the hydriodic acid formed is then titrated with decinormal soda, using methyl orange as an indicator.

Commercial iodine seldom contains any impurity but moisture; it is almost impossible to estimate the water by drying in the ordinary way. An easy method is to rub it up with five times its weight of pure dry mercury, adding a little alcohol. It is then dried for 12 hours, or until it ceases to lose weight, over sulphuric acid in a desiccator. This process is accurate to about 0·1 p.c., but most suitable for very damp iodine. Another method is to add a weighed quantity (about double the weight of the iodine) of zinc sheet in small pieces in a tared capsule, along with a little water, when the iodine is all converted into zinc iodide; the contents of the capsule are gradually evaporated to dryness and weighed, the weight then includes that of the dry iodine. It is better, however, in all cases to estimate the iodine by titration. The same may be said of the valuation of potassium iodide; but in this case it is often also necessary to estimate a small quantity of chloride which is always present; and silver nitrate is the best reagent for this purpose, as the chloride ought to represent so small a percentage as to be difficult of detection. Bromine as a rule need not be looked for. Should it be present, however, some other process must be employed. It is necessary to take at least 3 grams of the potassium iodide, and add to it not less than 3·1 grams of pure silver nitrate; the precipitate is digested in strong ammonia, then filtered off, washed, dried, and fused with the usual precautions. The solution is concentrated by evaporation, and the silver chloride precipitated by nitric acid. This gives accurate results, even when the potassium chloride is under 0·5 p.c.

For the determination of small proportions of chlorine and bromine in iodine, the following process is recommended by Tatlock and Thomson (J. Soc. Chem. Ind. 1905, 24, 187). 10 grams of the sample are triturated with 100 c.c. of water, and finely granulated zinc, or zinc-dust, is added in small portions, with agitation, until all the iodine is converted into zinc iodide. The temperature of the solution must not be allowed to rise sensibly during the process. The solution is now filtered, the residue washed two or three times, and to the filtrate 7 grams of pure sodium nitrite are added. The solution is carefully acidified with dilute sulphuric acid, the precipitated iodine is collected and washed two or three times with cold water, and the filtrate is agitated with benzene in a small separator. The aqueous layer is run into another small separator, mixed with a little more sodium nitrite and dilute sulphuric acid, and again shaken with benzene. To the aqueous solution excess of silver nitrate and some nitric acid are added, the liquid is heated to boiling, and the precipitate is collected on a weighed filter and well washed with hot water. A solution containing 2 grams of silver nitrate, 90 c.c. of water, and 10 c.c. of ammonia of sp.gr. 0·88 is prepared. About 60 c.c. of this solution are poured back and forward through the filter containing the precipitate, and the latter is finally washed with the remaining 40 c.c. The silver bromide on the filter is now washed with warm dilute nitric acid and with hot water, dried, and weighed. The ammoniacal filtrate is acidified with dilute nitric acid, and the precipitate of silver chloride is collected as usual. G. G. H.

IODIPIN, IODIVAL, IODLECITHIN, *v.* SYNTHETIC DRUGS.

IODOCAFFEIN *v.* SYNTHETIC DRUGS.

IODOFAN. Trade name for monoiododihydroxybenzene-formaldehyde.

IODOFORM and **SUBSTITUTES.** Iodoform (B.P. and U.S.P.), *tri-iodomethane* CHI_3 was discovered in 1822 by Serullas (Ann. Chim. Phys. [ii.] 20, 165), and Dumas in 1834 (*ibid.* [ii.] 56, 122) determined its exact composition. Serullas obtained it by acting on alcohol with iodine in presence of caustic or carbonated alkalis. The reaction may be stated thus:

$$CH_3{\cdot}CH_2{\cdot}OH+4I_2+6KOH$$
$$=CHI_3+HCOOK+5KI+5H_2O$$

Numerous other compounds (acetone, lactic acid, turpentine) containing the group

$$CH_3{\cdot}CO{\cdot}C \text{ or } CH_3{\cdot}CH(OH){\cdot}C$$

yield iodoform (Lieben, Annalen, Suppl. 7, 218 and 377). Methyl alcohol and acetic acid do not, when pure. The only practical sources are ethyl alcohol and acetone. Acetylides, acetylene mercuric chloride, acetylene (and coal-gas), also yield iodoform, Le Comte (J. Pharm. Chim. 1902 [vi.] 16, 297), but this source does not appear to have been used practically.

To prepare iodoform, Filhol (J. Pharm. Chim. [iii.] 7, 267) adds 1 part of alcohol to a solution of 2 parts of crystallised sodium carbonate in 10 parts of water and raises the temperature to 60°–80°. 1 part of powdered iodine is then *gradually* added, and when the liquid has become colourless, iodoform slowly forms and sinks to the bottom and may be removed by filtration. The filtrate is heated as before, another portion of sodium carbonate and alcohol added, and chlorine is led into the mixture to liberate iodine which has combined with the alkali. Another deposit of iodoform occurs, and the process may be repeated until the product represents nearly half the iodine employed. Another plan, suggested by Rother (Pharm. J. [iii.] 4, 594), is to warn the following mixture until it becomes colourless: iodine 32 parts, potassium carbonate 32 parts, 95 p.c. alcohol 16 parts, water 80 parts. The iodoform which is deposited is removed, and to the clear solution a mixture of potassium dichromate 2 to 3 parts, and hydrochloric acid 16 to 24 parts, is added to liberate iodine. After neutralising the solution with potassium carbonate, 32 parts more of that salt are added, together with 6 parts of iodine and 16 parts of alcohol, and the heat being maintained a second quantity of iodoform precipitates. This may be removed and the operation repeated several times (*cf.* Cornelius and Gille, J. Pharm. Chim. [iii.] 22, 196; Smith, Pharm. J. [iii.] 5, 211; Bell, *ibid.* [iii.] 12, 786; Günther, Arch. Pharm. [iii.] 25, 373). Iodoform can be prepared by the electrolysis of a solution of an iodide in the presence of alcohol, aldehyde, or acetone (Dingl. poly. J. 255, 88; J. Soc. Chem. Ind. 1885, 243; Foerster and Meves, J. pr. Chem. 1897, [ii.] 56, 353; Elbs and Herz, Zeitsch. Elektrochem 4, 113; Abbot, J. Phys. Chem. 1903, 84; Teeple, Amer. Chem. J. 1904, 26, 170. The last-named claims an almost quantitative yield). According to Suilhot and Raynaud (Bull. Soc. chim. [iii.] 1, 3) almost the whole of the iodine employed is obtained as iodoform when acetone is acted upon by what is possibly nascent potassium hypoiodite produced by treating potassium iodide with sodium hypochlorite. A slight excess of dilute solution of sodium hypochlorite is added to a mixture of potassium iodide 50 parts, acetone 6 parts, and sodium hydroxide 2 parts, dissolved in 1 to 2 parts of water. The reaction probably takes place thus:

$$(1)\ KI+NaClO=KIO+NaCl$$

$$(2)\ CH_3{\cdot}CO{\cdot}CH_3+3KIO$$
$$=CHI_3+CH_3COOK+2KHO$$

This process has been applied to the working of kelp, and is said to produce iodoform of a very high degree of purity (Pharm. J [iii.] 20, 423).

A novel method has been described by Chattaway and Baxter (Chem. Soc Trans. 1913, 103, 1896), in which acetone reacts with finely divided nitrogen iodide, prepared from iodine monochloride and ammonia. Tri-iodo acetone is first formed, and this is decomposed by water and by ammonia into iodoform, with acetic acid and acetamide respectively. Four-fifths of the iodine can be obtained as iodoform in one operation.

Iodoform crystallises in lemon-yellow hexagonal plates (according to Bardach, Chem. Zeit. 1911, 35, 11, it also forms thin needles and is consequently dimorphic). They melt at 119°, volatilise when heated, or better in a current of steam. It has a persistent and disagreeable odour. It is nearly insoluble in water, benzene, or light petroleum; 1 gram dissolves in 60 c.c. of alcohol, 80 c.c. of glycerine, 10 c.c. of chloroform, 7·5 c.c. of ether, 2·8 c.c. of carbon disulphide, and 34 c.c. of olive oil at 2·5°; also in 16 c.c. of boiling alcohol (U.S.P.). In the dry state iodoform is not acted on by sunlight; but in solution, with access of oxygen, it rapidly liberates free iodine (Humbert, J. Pharm. Chim. [iii.] 29, 352; Hebeler, Pharm. J. [iii.] 16, 1088; Daccomo, Gazz. chim. ital. 16, 247; Neuss and Schmidt, Pharm. J. [iii.] 19, 247; Fischer, Pharm. Zeit. 34, 31; Bougault, J. Pharm. Chim. [vi.] 8, 213). Its antiseptic properties have been attributed to the slow liberation of iodine. *In vitro* it is almost without effect; it would appear, however, that it acts differently in presence of pus at the temperature of the body. Iodine is, in this case, liberated which perhaps also attacks the toxins. Hamburger, de Haan, and Bubanovic (Proc. K. Akad. Wetensch. Amsterdam, 1911, 13, 982) state that even in excessively dilute solution it has a favourable effect on phagocytoses; the action is not due to iodine antisepsis, but rather to a physical effect (surface tension?) of intact iodoform on leucocytes.

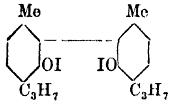
Heated in sealed tubes to 150°, or with sodium ethoxide or alcoholic potash, iodoform forms methylene iodide CH_2I_2. The zinc-copper couple, finely divided silver, and other metals reduce it to acetylene.

Iodoform is best detected and isolated by steam distillation from slightly acid solution (Stortenbeker, Rec. trav. chim. 1905, 24, 66). The distillate is extracted with ether, which is allowed to evaporate in the dark. Better crystals, for microscopic examination, may then be obtained by recrystallisation from glacial acetic acid. The red precipitate, formed by heating an alcoholic iodoform solution with sodium phenoxide, is, according to Stortenbeker, not characteristic, for it is also given by chloroform and bromoform. The estimation of iodoform may be carried out by digesting with silver nitrate and weighing the silver iodide, or titrating the excess by Volhard's method. Detection of adulteration (Kremel, Pharm. Post. 21, 213). Picric acid has been used, and is separated by shaking the ethereal solution with alkali. Assay of iodoform (Meillière, Chem. Zentr. 1897, ii. 140).

Iodoform is not now used so much as in the early days of antiseptic wound treatment, but as a dry powder which can be scattered it has considerable advantages. During the recent war it was used extensively and very successfully as bismuth-iodoform-petroleum-paste ('B.I.P.P.') suggested by Morison (Lancet, 1916, ii 268), and consisting of bismuth subnitrate or carbonate with 1–2 parts of iodoform and enough pure liquid paraffin to make a thick paste. The odour, and to some extent the poisonous properties, of iodoform have given rise to a host of substitutes, all apparently inferior. Attempts have been made to mask the odour by addition of coumarin (2 p.c.) or of oil of peppermint (1 p.c.) + phenol (0·5 p.c.). Other attempts depend on its combination with hexamethylene tetramine or with protein to form non-volatile compounds. The oldest substitute is *iodol* or tetra-iodopyrrole, C_4HNI_4, formed by the action of iodine on potassium pyrrole (Ciamician and Dennstedt, Ber. 15, 2582; Ciamician and Silber, *ibid.* 18, 1766; 19 Ref. 327; 20 Ref. 123). It crystallises from alcohol in light yellow needles, decomposing at 140°–150° and is odourless. Like iodoform it is practically insoluble in water, and liberates iodine in contact with the tissues. Gently warmed with sulphuric acid it gives an intense green solution, gradually changing to dull violet and brown.

Di-iodoform, tetra-iodo-ethylene, is obtained from calcium carbide and iodine, or from iodine and di-iodo-acetylene (Biltz, Ber. 1897, 30, 1200; Biltz and Kuppers, *ibid.* 1904, 37, 4412), but is too unstable and too heavy to displace iodoform in wound treatment.

A number of aromatic iodine derivatives have been suggested but those with iodine in the benzene ring do not split it off in contact with the tissues and hence are only antiseptic like other aromatic compounds. Such are iodohydroxyquinoline sulphonic acid (*loretin*), tetra-iodo-phenolphthalein (*nosophen*), tri-iodometacresol (*losophan*) and iodoparaphenol-sulphonic acid (*sozojodol*); *p*-Iodo-anisol (*isoform*) seems to be the best of this group. When the iodine is attached to oxygen as in hypoiodites of phenols, it is more readily split off, as in dithymoldiiodide (*aristol*)



and di-isobutyl-*o*-cresol iodide (*europhen*).

The physical properties and therapeutic effects of iodoform also belong to certain bismuth compounds, *e.g.* bismuth tribromophenoxide (*xeroform*) and bismuth oxy-iodogallate (*airol*). Another class consists of inert powders with which iodine is loosely combined or merely mixed physically, *e.g.* *novojodin*, an addition product of iodine to hexamethylenetetramine containing 60 p.c. of iodine; '*Jod-salusil*' (Chem. Zentr. 1917, ii. 189) is finely divided silicic acid, prepared by electrosmosis, mixed with 1 p.c. of free iodine. Iodide of starch has occasionally been recommended. *See further*, SYNTHETIC DRUGS. G. B.

IODOFORMAL *v.* SYNTHETIC DRUGS.

IODOFORMIN $C_6H_{12}N_4I_4$ is prepared by adding an alcoholic solution of iodine to ammonia and formaldehyde mixed in molecular proportions when iodoformin falls as a brown pulverulent precipitate (*v.* SYNTHETIC DRUGS).

IODOFORMOGEN *v.* SYNTHETIC DRUGS.

IODOGLIADIN. A combination of iodine and gliadin, a protein contained in wheat.

IODOGLOBIN. Syn. for Di-iodotyrosine.

IODOHYDRIN. (*iothion*), Syn. for di-iodo*iso*propyl alcohol.

IODOKOL *v.* SYNTHETIC DRUGS.

IODOLE *v.* IODOFORM.

IODOLEN, IODOLIN, IODOGALLICIN, IODOPHENIN, IODOZOL, *v.* SYNTHETIC DRUGS.

IODOLYSIN. An additive compound of an alcoholic iodide with thiosinamine. Used in relaxing scar-tissue.

IODOMENIN *v.* SYNTHETIC DRUGS.

IODOMETRY *v.* ANALYSIS, VOLUMETRIC.

IODOPHENIN. Trade name for *p*-acetohydriodotetraiodide $(C_{10}H_{13}O_2N)_2HI.I_4$ (Emery).

IODOPYRINE. A pharmaceutical preparation made by adding a solution of iodine in potassium iodide to an aqueous solution of antipyrine containing sodium acetate.

IODOTHEOBROMIN, IODYLIN, IODYLOFORM *v.* SYNTHETIC DRUGS.

IODOTHION *v.* SYNTHETIC DRUGS.

IODOTHYRINE *v.* THYROID GLAND.

IODOZOL. Trade name for di-iodo-*p*-phenol sulphonic acid.

IODYRITE, or **Iodargyrite.** A mineral composed of silver iodide (AgI) crystallising in the rhombohedral system. Distinctly developed crystals are small and comparatively rare; they possess a perfect cleavage parallel to the basal plane, on which the lustre is pearly, and are very soft (H.=1) and readily distorted. Their pale sulphur-yellow is not darkened by exposure to sunlight. Sp.gr. 5·51. At a temperature of 146°, the material becomes optically isotropic and cubic, reverting on cooling into the birefringent rhombohedral form.

The mineral occurs in the upper oxidised zones of certain silver-bearing veins, and when found in quantity, as at Broken Hill in New South Wales, in Chile and Mexico, and at Tonopah in Nevada, it is an important ore of silver (Ag, 45·97 p.c.). Some of the silver-ore formerly mined at Broken Hill consisted of white kaolin enclosing films and specks of iodyrite.

Miersite is a rare cubic form of silver iodide with copper iodide (4AgI·CuI) from Broken Hill, New South Wales (L. J. Spencer, Min. Mag. 1901, 13, 41; G. T. Prior, *l.c.* 188). L. J. S.

IOLITE, dichroite or **cordierite.** A silicate of aluminium and magnesium with some ferrous iron replacing magnesium $H_2(Mg,Fe)_4Al_8Si_{10}O_{37}$ or perhaps $Mg_2Al_2(AlO)_2Si_5O_{16}$ crystallised in the orthorhombic system. It occurs as a constituent of certain gneisses and granites, and is readily altered to mica, pseudomorphs being more common than the fresh mineral. In its physical characters it presents a close resemblance to quartz, namely, in the glassy conchoidal fracture, hardness (H. 7-7½), density (sp gr. 2·60-2·66), refractive index (1·54) and double refraction. The mineral is of interest on account of its strongly marked pleochroism (except in thin sections); viewed in the three directions of the crystallographic axes it shows dark blue, light blue, and pale yellow colours. It is occasionally used as a gem-stone; and to show the pleochroism to advantage it is sometimes cut in a cuboidal form and mounted on a swivel. When cut as a faceted gem this should be so orientated that the front facet will be perpendicular to the direction in which the deep blue colour is seen: such stones are known to jewellers as 'lynx-sapphire' or 'water-sapphire.' Material of gem-quality comes from the gem-gravels of Ceylon, Orijarvi in Finland, Haddam in Connecticut, and Mt. Bity in Madagascar. L. J. S.

IONIUM. Sym Io. At.wt. 230. A radioactive element, discovered by Boltwood in uranium minerals (Boltwood, Amer. J. Sci. 1907, 24, 370; *cf.* Hahn, Ber. 1907, 40, 4415). The results obtained by Boltwood and Hahn were confirmed by Marckwald and Keetman (Ber. 1908, 41, 49), who were unable to separate ionium from thorium, an element which it closely resembles. Ionium occurs, however, associated with actinium, in many of the uranium group of minerals in the absence of thorium (Szilárd, Le Radium, 1909, 6, 80).

Highly active preparations of ionium may be obtained from carnotite as follows (Boltwood) Amer. J. Sci. 1908, 25, 365). The ore is dissolved in hydrochloric acid and several grams of the chlorides of the cerite earths added. The earths are separated as oxalates, converted into chlorides, and precipitated with sodium thiosulphate. The latter procedure is repeated several times, when a product is obtained having a radioactivity several thousand times as great as that of an equal weight of pure uranium.

The residues obtained in working up uranium ores containing little thorium may be precipitated in strongly acid solution with hydrofluoric acid. The precipitated fluorides are converted into sulphates, and from the aqueous solution of these, ionium and thorium are quantitatively precipitated by adding zinc hydroxide. The precipitate is dissolved in hydrochloric acid and the solution precipitated with oxalic acid. The oxalate thus obtained contains the ionium, and has an activity 200 times as large as that of metallic uranium (Keetman, Jahrb. Radioaktiv. Elektronik. 1909, 6, 265).

Ionium emits α-rays, which have a range in air of only 2·8 cms.; it also emits β-rays. It produces no emanation. The life of ionium is at least as long as that of radium (*cf.* Soddy, Le Radium, 1910, 7, 295).

According to Boltwood, ionium is the direct parent of radium, and according to Keetman (*l.c.*), does not change directly into actinium.

Thorium-ionium oxalate has a very high and constant activity, and may with advantage be utilised in testing the constancy of electrometers and for determining capacities (Keetman, *l.c.*).

IONONES *v.* KETONES.

IPECACUANHA. *Ipecacuanha Root. Racine d'Ipecacuanha*, Fr.; *Brechwurzel*, Ger. Ipecacuanha is the root of *Psychotria Ipecacuanha*, Stokes, also known as *Cephaelis Ipecacuanha*, A. Richard, and *Uragoga Ipecacuanha*, Baillon (N. O. Rubiaceæ), a low soft-wooded shrub indigenous to Brazil. Three commercial varieties of this root are distinguished: (1) Rio or Matto Grosso, (2) Minas, which is derived from the same plant, cultivated in the province of Minas Geraes in Brazil, and (3) Indian or Johore, also derived from the same plant, cultivated in the Straits Settlements.

Rio Ipecacuanha occurs in commerce in reddish-brown or dark brown pieces seldom exceeding 15 cm. in length, and 6 mm. in thickness; it has a thick bark, transversely corrugated or ringed—the corrugations often penetrating to the woody interior—and minutely wrinkled longitudinally. The Minas variety resembles it closely, whilst the Johore drug is rather larger than the Brazilian root.

The B.P. 1914 recognises only *Psychotria Ipecacuanha* as the official source of ipecacuanha, but the U.S.P. 1916 authorises the use of the root of *Cephaelis acuminata*, Karsten, also. This is known commercially as Carthagena or Colombian Ipecacuanha, and is usually lighter in colour and rather larger than the Brazilian root.

For information on the ipecacuanhas of English commerce and others sometimes substituted for them, *cf.* E. M. Holmes, Yearbk. Pharm. 1893, 402.

The drug was first introduced into Europe from Brazil about the close of the seventeenth century as a remedy for dysentery, and since that period it has always retained a place in *materia medica.* It is employed as an expectorant, as an emetic, and in the treatment of dysentery. Applied locally the powdered root is an irritant, and in large doses it is poisonous. (*Cf.* Pereira, Mat. Med. 1853, 2, 1591; Fluck. a. Hanb. 370.) It is administered in the state of powder—for instance, admixed with opium and potassium sulphate in the well-known Dover's Powder—made into pills, or in vinous solution. In recent years, however, the salts of emetine have been largely used in its place in the treatment of amœbic dysentery.

The most important constituent of ipecacuanha is the alkaloid *emetine*, which is associated with several other bases closely related to it in structure. The term emetine was first applied by Pelletier and Magendie (Ann. Chim. 1817, [ii.] 4, 172) to a crude preparation of the total alkaloids of ipecacuanha, and was used subsequently by numerous authors to designate various purified preparations of the alkaloids. The earlier researches may be traced by reference to the papers of Paul and Cownley, and only one need be mentioned here, namely, that of Glénard (Ann. Chim. 1876, [v.] 8, 233), who succeeded in preparing emetine hydrochloride in a crystalline state by a fortunate choice of procedure. The first real advance in the study of these alkaloids was made by Paul and Cownley (Pharm. J. 1894, [iii.] 25, 111), who showed that the portion soluble in ether could be separated into two fractions by extraction with aqueous sodium hydroxide, when the ethereal solution contained a nonphenolic alkaloid for which the name *emetine* was retained, whilst the alkaline liquor contained a crystalline alkaloid which was termed *cephaeline.* Subsequently (Pharm. J. 1894, [iii.] 25, 690) they isolated a third alkaloid, *psychotrine*, from the root. Many years later O. Hesse (Annalen, 1914, 405, 1) described two more alkaloids of ipecacuanha, *ipecamine* and *hydroipecamine*, but these are probably not homogenous substances (*cf.* Pyman, Chem. Soc. Trans. 1917, 111, 49). More recently Pyman (*l.c.*) isolated two new alkaloids of ipecacuanha, one being the *o-methyl ether of psychotrine*, whilst the other was termed *emetamine.*

Neglecting publications previous to those of Paul and Cownley, the chemistry of these alkaloids has been studied by Paul and Cownley, Pharm. J. 1893, [iii.] 24, 61; 1894, [iii.] 25, 111, 373, 641, 690; 1895, [iv.] 1, 1, 321; the same with Hesse, Pharm. J. 1898, [iv.] 7, 98; Frerichs and de Fuentes Tapis, Arch. Pharm. 1902, 240, 390; Keller, Arch. Pharm. 1911, 249, 512; 1913, 251, 701; 1917, 255, 75; Carr and Pyman, Chem. Soc. Proc. 1913, 29, 226; Chem. Soc. Trans. 1914, 105, 1591; Hesse, Annalen, 1914, 405, 1; Windaus and Hermanns, Ber. 1914, 47, 1470; Pyman, Chem. Soc. Trans. 1917, 111, 419; 1918, 113, 222; and Karrer, Ber. 1916, 49, 2057; 1917, 50, 582. Patents have been taken out by W. G. Whiffen, D. R. P. 99090 (1897) for the purification of emetine by crystallisation of the hydrobromide; by Chem. Werke vorm. Dr. Heinr. Byk., D. R. P. 267219 (1912) for the extraction of the alkaloids from the root by means of chloroform mixed with alcoholic hydrogen chloride; by H. S. Wellcome, F. H. Carr and F. L. Pyman, Eng. Pats. 14677 and 17483 (1913) for the preparation of emetine by the methylation of cephaeline by means of dimethyl sulphate and sodium methyl sulphate respectively; by Farbw. vorm. Meister, Lucius und Bruning, D. R. P. 298678 (1916) for the preparation of emetine by the methylation of cephaeline by means of diazomethane; by J. W. Meader, Eng. Pats. 11717, 11718, 11719 (1915); 103881, 104652, 105722 (1916); U.S. Pat. 1209575 (1917), and by Farbw. vorm. Meister, Lucius und Brüning, D. R. P. 301498 (1915) for the preparation of homologues of emetine by the alkylation of cephaeline with derivatives of alcohols other than methyl alcohol.

Isolation of the alkaloids.—The total alkaloids extracted from the powdered root by means of alcohol, amyl alcohol (Paul and Cownley), or a mixture of benzene with light petroleum (Hesse) are dissolved in dilute hydrochloric acid, basified with ammonia, and extracted with ether which removes all the known alkaloids except psychotrine; this is extracted from the mother liquor by chloroform and crystallised from moist acetone. The ethereal solution is extracted with dilute aqueous sodium hydroxide, from which cephaeline can be extracted by means of ether after the addition of ammonium chloride; on concentrating this ethereal solution cephaeline separates in long colourless needles. The ethereal solution containing the nonphenolic alkaloids is concentrated and the residue converted into the hydrochloride (Paul and Cownley), hydrobromide (Whiffen), or hydriodide (Karrer), when the emetine salt separates in a crystalline form. After removing the emetine, the remaining alkaloids are converted into acid oxalates in alcoholic solution, when the crystalline acid oxalates of *O*-methylpsychotrine and emetamine are deposited; these are separated by fractional extraction from their chloroform solutions by dilute acids.

Properties.—*Emetine* has the formula

$$C_{29}H_{40}O_4N_2$$

(Carr and Pyman; Karrer) being the monomethyl ether of cephaeline, for which the formula $C_{28}H_{38}O_4N_2$ is accepted. Other formulæ proposed for emetine are $C_{30}H_{44}O_4N_2$ (Paul and Cownley), which is employed in the U.S.P 1916, $C_{30}H_{42}O_4N_2$ (Hesse, 1898) and $C_{30}H_{40}O_5N_2$ (Hesse, 1914). It contains four methoxyl groups, one tertiary nitrogen atom common to two rings, and one secondary nitrogen atom contained in a ring. The largest fragment of the molecule so far obtained on oxidation is 6 : 7-dimethoxy*iso*quinoline-1-carboxylic acid, the formation of which shows that emetine is a derivative of *iso*quinoline

Emetine is amorphous and colourless, but turns yellow on warming or keeping. It melts at 74° (corr.) and has $[\alpha]_D -50°$ in chloroform (c =2). It is sparingly soluble in water or light petroleum, but readily so in alcohol, ether, or chloroform. It is a diacidic base forming neutral salts with two equivalents of acids. The hydrochloride, hydrobromide, and the double iodide of emetine and bismuth are employed in medicine.

The hydrochloride B,2HCl contains water of crystallisation varying from 3 to $8H_2O$. It forms colourless woolly needles, which after drying at 100°, melt indefinitely at 235°–255° (corr.). Its specific rotatory power in aqueous solution varies with the concentration from $[\alpha]_D +11°$ (c.=1) to $[\alpha]_D +21°$ (c.=8), calculated for the anhydrous salt. It is readily soluble in warm water (about 1 in 4 at 37°C.), but more sparingly so in cold water (about 1 in 7 at 25°C., and 1 in 11 at 15°C.), giving solutions which are neutral to litmus. It is official in the U.S.P. 1916. This salt and also the hydrobromide are given by the mouth or hypodermically in doses up to 1 grain in the treatment of amœbic dysentery.

The hydrobromide $B,2HBr,4H_2O$ forms colourless needles, which melt indefinitely at 245°–265° (corr.). It is readily soluble in hot, sparingly so in cold water (1 : 50).

Emetine bismuthous iodide, prepared by the addition of Dragendorff's reagent (potassium bismuthous iodide) to an aqueous solution of an emetine salt, is a dull scarlet powder, almost insoluble in water, approximating in composition to $B,2HI,2BiI_3$. It is given orally in amœbic dysentery, and is stated to cause less nausea than the soluble salts, since it is almost insoluble in the acid contents of the stomach, exerting its full effect only in contact with the alkaline juices of the intestines.

The sulphate, nitrate and hydriodide are also crystalline, the last two being sparingly soluble in water.

Cephaeline $C_{28}H_{38}O_4N_2$ forms colourless needles from ether, melting at 115°–116° (corr.). $[\alpha]_D -43°$ in chloroform (c. =2). Sparingly soluble in water, ether, or light petroleum; easily so in alcohol or chloroform. The hydrochloride, B,2HCl, 5 to 7 H_2O forms colourless prisms, easily soluble in water, melts at 245°–270° (corr.) when anhydrous, and is dextrorotatory. The hydrobromide is also crystalline.

Psychotrine $C_{28}H_{36}O_4N_2,4H_2O$ crystallises from moist acetone in yellow prisms having a blue fluorescence. M.p. (anhydrous) 124°–126° (corr.) $[\alpha]_D +69°$ in 99 p.c. alcohol (c. =2). Forms crystalline dextrorotatory salts with H_2SO_4,HI and HNO_3. Yields cephaeline and an isomeride on reduction.

O-**Methylpsychotrine** $C_{29}H_{38}O_4N_2$ is amorphous and has $[\alpha]_D +46°$ in chloroform (c. =2). Forms crystalline dextrorotatory salts with H_2SO_4,HBr and oxalic acid. Yields emetine and an isomeride on reduction.

Emetamine $C_{29}H_{36}O_4N_2$ (or $C_{30}H_{36}O_4N_2$) forms colourless needles from ethyl acetate. M.p. 155°–156° (corr.) $[\alpha]_D +10°$ in chloroform (c.=4). Forms crystalline lævorotatory salts with HBr, and oxalic acid.

Detection and estimation. A characteristic reaction of the alkaloids is the yellow or orange colour produced by the action of bleaching powder and acetic acid (Power, Pharm. J. 1877, [iii.] 8, 344). Froehde's reagent gives a grass-green colour with emetine, and a purple colour with cephaeline; this distinction is utilised in a test devised to detect the presence of cephaeline in commercial emetine hydrochloride (U.S.P. 1916).

The official methods of assay of ipecacuanha consist in the estimation of the total ether-soluble alkaloids. The B.P. 1914 requires a content of 2 p.c. estimated gravimetrically, whilst the U.S.P. 1916 requires a content of 1·75 p.c. estimated by titration with standard acid. The nonphenolic and phenolic portions of the ether-soluble alkaloids may be separated and estimated similarly. For a review of the methods of assay, *see* Frerichs and Tapis (Arch. Pharm. 1902, 240, 390).

The root contains 1·5–2·5 p.c. of total alkaloids, consisting mainly of emetine and cephaeline, with 0·04–0·06 p.c. of psychotrine, 0·015–0·033 p.c. of methylpsychotrine, and 0·002–0·006 p.c. of emetamine; the proportions of emetine and cephaeline in the different commercial varieties are given by Paul and Cownley, Pharm. J. 1896, [iv.] 2, 321; 1903, [iv.] 15, 256; Umney and Swinton, Yearbk. Pharm. 1899, 348; Carr and Reynolds, Pharm. J. 1908, [iv.] 26, 542, and Hesse, Annalen, 1914, 405, 1.

Non-alkaloidal constituents.—Besides the alkaloids, few definite compounds have been isolated from the root. A crystalline yellow colouring matter, *erythrocephaelein*, forming purple-red compounds with alkalis was isolated by Podwyszotzky, Pharm. J. 1880, [iii.] 10, 642. The presence of *choline* was detected by H. Kunz, Arch. Pharm. 1887, [iii.] 25, 461. A colourless glucoside, *ipecacuanhin*, was isolated by Finnemore and Braithwaite, Pharm. J. 1912, [iv.] 35, 136, and a *phytosterol*, m.p. 160°–162° (corr.) by Carr and Pyman. The root contains a large amount of starch and up to 5 p.c. of ash.

F. L. P.

IPOMEA *v.* Scammony. art. Gum resins.

IRETOL *v.* Phenol and its homologues.

IRIDIN *v.* Glucosides.

IRIDIUM. Sym. Ir. At wt. 193·04.

The occurrence of this metal and the properties of its principal alloys with platinum will be described under Platinum. Its principal source is the osmiridium which is left after treatment of crude platinum with *aqua regia*.

The cleaning and methods of attack of the insoluble osmiridium are also given under Platinum. Briefly, iridium is freed from ruthenium and osmium by distilling in chlorine after an alkaline fusion, and from rhodium and palladium by the difference of solubility of the double chlorides with potassium or ammonium. It may be freed from platinum either by melting the metal with ten times its weight of lead, parting in nitric acid and boiling the residue in *aqua regia*, or by reducing the acidified chloride solution with H_2S, SO_2, ferrous salts, nitrites, oxalic acid or other suitable reagent, precipitating the unattacked $PtCl_4$ with ammonium or potassium chloride and either re-oxidising the solution to precipitate the chloroiridate or crystallising the chloroiridite by evaporation. The ammonium salt has the advantage over the potassium salt that it may be decomposed to leave a base-free solution by boiling with *aqua regia*, or it may be calcined in a closed vessel to leave the metal as sponge. If calcined in an open vessel the residue may subsequently be reduced to metal by hydrogen at a gentle heat.

The metal is best converted into the soluble chloride by heating in chlorine with salt or dehydrated barium chloride. In the latter case the barium may be removed from the solution by sulphuric acid.

Iridium sponge is oxidised but not dissolved by fused bisulphate. Traces of osmium in iridium sponge may be detected by bringing some of it on a piece of platinum foil into a Bunsen burner flame alternately in the reducing and oxidising zones, when bright flashes or sparks are observed; but the characteristic smell of OsO_4 on heating in air is reliable and sensitive.

On account of their extreme hardness, the native grains of osmiridium are employed as such for tipping the points of gold nibs, but only a small proportion even of the few grains which occur with ordinary crude platinum are suitable for the purpose. A small quantity of osmiridium is used for pivots, &c., of watches and scientific instruments, but practically the whole is worked up for the production of iridium, which is mainly employed in alloy with platinum, as described under Platinum.

Melted iridium may be cast in a lime mould, and the ingot forged or rolled at a bright red heat. Sheets suitable for dishes or crucibles may thus be prepared, but the metal, even if pure, is very hard and brittle when cold. Thin foil may, however, be rolled out, and has found an application in an electric meter as an electrode in a solution of a mercury salt. The forged metal becomes superficially oxidised at a red heat in air or oxygen, but the blue tint, not so pronounced as the 'temper' colours of steel, disappears on further heating. Acids, however, have no action on it, nor have certain fused base metals. For further details *see* Crookes, Proc. Roy. Soc. 1908, A. 80, 535.

Iridium is a white metal as bright as steel, having a sp gr. of 22·39 (G. Matthey), and melting at about 1950°; 2150°–2250° (J. Ind. Eng. Chem. 1911, 3, 354).

The compact metal, like osmiridium, may be broken down by melting with excess of zinc, in which, of course, it sinks, and then boiling away the whole of the zinc. Or the zinc may be kept as long as is necessary just below its boiling-point (918°), and then dissolved away by acid (Deville and Debray, Ann. de Ch. et de Ph. 1859, [3] 56, 439).

At a dull red heat iridium combines with fluorine, chlorine, or oxygen. It also combines with sulphur when heated, and gives a readily fusible compound with phosphorus, which is decomposed at a white heat.

Colloidal iridium may be obtained by mixing iridium chloride with lysalbic acid and concentrated soda, and subsequently dialysing the mixture (Paal and Amberger, Ber. 1904, 37, 124); or by reducing iridium chloride with hydrazine hydrate in the presence of gum arabic solution (Gutbier and Hoffmeier, J. pr. Chem. 1905, [ii.] 71, 452). It is a catalyst, but is not as powerful as colloidal platinum. *See* Paal, Biebler & Steyer, Ber. 1917, 50, 722.

For its action in inducing the catalytic oxidation of carbon monoxide by oxygen, *see* Paal, Ber. 1916, 49, 548.

Iridium black is a complex mixture containing varying proportions of the metal and its oxides, obtained by reducing iridium salts with alcohol, formic acid, or formaldehyde. The black powder thus formed is washed with water and dried *in vacuó* (Böttger, J. pr. Chem. 1834, 3, 276). It has properties similar to, but more powerful than, those of platinum black. It absorbs gases and has the property of inducing chemical action, as, for instance, the combustion of hydrogen and of alcohol, the transformation of chlorine, iodine, or bromine water into halogen acid and oxygen, the decomposition of hypochlorites, and so forth (Schönbein, Ann. Chim. 1856, [iv.] 7, 103, 113).

Although the black iridium oxide is a valued pigment for china, the commercial use of iridium for that or other purposes other than as metal or in alloys, is practically *nil*, as the demand for the metal as such exceeds the supply. For the same reason, none of the large variety of salts which iridium forms, is of technological interest.

IRIDIUM COMPOUNDS.

According to Wöhler and Witzmann (Zeitsch. anorg. Chem. 1908, 57, 323; *see* also Zeitsch. Elektrochem. 1908, 14, 97), the oxide IrO does not exist under ordinary conditions, and all the known oxides are unstable at 800°–1000°.

Iridium dioxide IrO_2 is best prepared by the action of alkali on a hot solution of sodium iridichloride Na_2IrCl_2, the sesquioxide first formed being oxidised to dioxide by a current of oxygen. The oxide is then dried in a current of carbon dioxide at 200°, after which it is boiled with alkali and then with sulphuric acid. The anhydrous dioxide and also the one containing 2 mols. H_2O is black. When freshly precipitated it is more readily soluble in acids and alkalis than when dried.

The solution obtained by the action of potash or sodium iridichloride in the cold, ultimately becomes violet in colour and contains the dioxide in colloidal form; after a time a violet modification of the dioxide separates, and on boiling, the solution becomes blue. The blue and green solutions of the dioxide in hydrochloric acid also contain the dioxide in colloidal solution.

Iridium sesquioxide Ir_2O_3 is obtained by mixing air-free hot solutions of sodium iridium trichloride $Na_3IrCl_6,12H_2O$, and potash in a current of carbon dioxide. The mixture is evaporated to dryness and heated to redness in a current of the same gas, after which it is purified in the same way as the dioxide. With hydrochloric acid this oxide also gives a colloidal solution. Like the dioxide, its properties depend on the proportion of water it contains. The sesquioxide imparts a fine black colour to porcelain after firing, and when mixed with zinc oxide it yields a grey tint.

Iridium trioxide is so unstable that it has not been obtained pure.

Iridium trihydroxide $Ir(OH)_3$ is a yellowish-green substance which dissolves in alkalis and oxidises rapidly in the air, forming

Iridium tetrahydroxide $Ir(OH)_4$, a heavy indigo-blue powder, which becomes green, then brown on heating (Joly and Leidié, Compt. rend. 1895, 120, 1341; Gutbier and Riess, Ber. 1909, 42, 3905).

Iridous chloride $IrCl_2$ is a green, insoluble mass, formed when chlorine is passed over spongy iridium or when the tetrachloride is heated.

Iridium trichloride $IrCl_3$ is a light, insoluble, olive-green powder prepared by heating one of its double salts with sulphuric acid, and also by other methods (Antony, Gazz. chim. ital. 1893, 23, i. 184). It forms complex compounds with the chlorides of phosphorus and arsenic (Geisenheimer, Compt. rend. 1890, 110, 1004, 1336), and double salts with metallic chlorides.

The most important of these are the potassium salt, $K_3IrCl_6,3H_2O$, big rhombic prisms, efflorescent in air and losing 9·45 p.c. at 18°; the ammonium salt $2(NH_4)_3IrCl_6,3H_2O$ and the sodium salt $Na_3IrCl_6,12H_2O$, large dark olive prisms, soluble in alcohol and melting at 50°.

Iridium tetrachloride $IrCl_4$ may be obtained by heating ammonium iridichloride in chlorine, or by dissolving the finely divided metal in *aqua regia*, or the blue hydroxide in hydrochloric acid. It loses chlorine at 50° and is readily converted by heat into $IrCl_3$. It forms double chlorides of the type M_2IrCl_6 with the alkali metal chlorides and with alkylamines. The potassium salt K_2IrCl_6 and the ammonium salt $(NH_4)_2IrCl_6$ both form small black octahedra, slightly soluble in water and almost insoluble in potassium or ammonium chloride solutions, like the corresponding platinum salts. The sodium salt $Na_2IrCl_6,6H_2O$ is also similar to the platinum salt, except in colour, and is freely soluble, as also is the barium salt (Rimbach and Korten, Zeitsch. anorg. Chem. 1907, 52, 406; Delépine, Compt. rend. 1909, 149, 1072; *ibid.* 1908, 146, 1267; Vézes, *ibid.* 1392; Gutbier, Zeitsch. physikal. Chem. 1909, 69, 304; Gutbier and Riess, *l.c.*). The iridichlorides, when reduced, yield the iridiochlorides Similar bromides and iodides of iridium also exist. *See also* Delépine, Bull. Soc. chim. 1914, [iv.] 15, 231, 267, 438, 505.

Iridium forms ammonium or ammino derivatives similar in constitution to the platinum compounds and corresponding to the chlorides $IrCl_2$, $IrCl_4$; also a series of compounds corresponding to $IrCl_3$, and analogous to the cobaltic, chromic, and rhodic compounds.

When iridium chloride is treated with ammonia, double salts $Ir(NH_3)_3Cl_3$,

$$Ir(NH_3)_4,Cl_3,H_2O,$$

and $Ir(NH_3)_5Cl_3,H_2O$ are formed. Iridium ammonia chlorohydroxide, sulphate, thionate, oxalate, nitrate, and a number of halide derivatives are also known (Palmaer, Zeitsch. anorg. Chem. 1895, 10, 320; *ibid.* 1896, 13, 211; *see* also Mylius and Dietz, Ber. 1898, 31, 3187).

Complex iridium nitrites and their chloro and oxalic acid derivatives have been prepared (Joly and Leidié, Compt. rend. 1895, 120, 1341; Leidié, *ibid.* 1902, 134, 1582; Bull. Soc. chim. 1902, [iii.] 27, 936; Vézes and Duffour, *ibid.* 1910, [iv.] 7, 507, 512; Miolati and Gialdini, Atti. R. Accad. Lincei, 1902, [v.] 11, ii. 151; Werner and Vries, Annalen, 1908, 364, 77).

Iridicyanides resemble the ferricyanides and are described by Martius (*ibid.* 1861, 117, 357; *see* also Rimbach and Korten, Zeitsch. anorg. Chem. 1907, 52, 406).

Iridium sulphides IrS, Ir_2S_3, IrS_2 (Antony, Gazz. chim. ital. 1893, 23, i. 184, 190), and the ammonium pentadecasulphide $(NH_4)_3IrS_{15}$ (Hofmann and Höchtlen, Ber. 1904, 37, 245) are known.

Iridium sulphate $Ir(SO_4)_2$ is a yellow-brown mass which when warmed with sulphuric acid is reduced, giving a green solution of the sesquisulphate $Ir_2(SO_4)_3,6H_2O$ (Rimbach and Korten, *l.c.*; also Lecoq de Boisbaudran, Compt. rend. 1883, 96, 1406 and 1551).

Iridium sesquisulphate forms alums with ammonium, thallium, and the alkali metals, of the type $Ir_2(SO_4)_3{\cdot}M_2SO_4,24H_2O$ (Marino, Zeitsch anorg. Chem. 1904, 42, 213; Rimbach and Korten, *l.c.*; Delépine, Compt. rend. 1906, 142, 637). It also forms sulphates of the type

$$Ir(SO_4M')_3,H_2O\ (?)\ \text{or}\ Ir_2(SO_4)_3{\cdot}3M_2SO_4,H_2O$$

which are bluish-green in colour, and are decomposed by ammonia and alkali hydroxides with precipitation of a violet oxide of iridium. The contained sulphuric acid is not precipitated by barium (Delépine, Compt. rend. 1906, 142, 1525).

According to Delépine iridium forms two series of disulphates: (1) green salts, generally acidic, derived from the acid

$$H_2[Ir(SO_4)_2(OH)H_2O]$$

(2) reddish-brown basic salts derived from the acid $H_3[Ir(SO_4)_2(OH)_2]$ (Compt. rend. 1909, 149, 785). He has also obtained green pyridine derivatives (*ibid.* 1910, 151, 878).

Double salts of *iridous sulphite* have been described by Seubert (Ber. 1898, 11, 1761).

Iridium selenide (Chabrié and Bouchonnet, Compt. rend. 1903, 137, 1059); *oxalates* (Gialdini, Atti. R. Accad. Lincei, 1907, [v.] 16, ii. 551, 648; Vézes and Duffour, Bull. Soc. chim. 1907, [iv.] 5, 869, 872); *phosphor halides* (Strecker and Schurigin, Ber. 1909, 42, 1768); and *mercaptide* (Hofmann and Rabe, Zeitsch. anorg. Chem. 1897, 14, 293) are known. A. J. W.

IRIDOSMINE or **OSMIRIDIUM.** A native alloy of iridium and osmium crystallised in the rhombohedral system. Analyses show the following range in composition: Ir 10·0–77·2, Os 17·2–80·0, Pt 0–10·1, Rh 0–17·2, Ru 0–8·9, Fe 0–1·5, Cu 0–0·9 p.c., Pd traces. Iridium and osmium replace one another isomorphously, the former usually predominating, and the names *nevyanskite* (osmiridium) and *sysertskite* or sisserskite (iridosmium) are applied to members towards the two ends of the series respectively. Crystals have the form of hexagonal plates, which possess a perfect basal cleavage; but more often the mineral is found as small flattened grains of irregular outline. Nuggets consisting of an aggregate of scales, and weighing up to 60 grams, have been found in Tasmania. The material is tin-white to lead-grey with bright metallic lustre, the colour being lighter in nevyanskite and darker in sysertskite. It is somewhat brittle or only slightly malleable, H. 6½–7; sp.gr. 18·6–21·6. It is unattacked by aqua regia; and in the treatment of crude platinum (with which iridosmine is often associated) it remains in the residues. At a high temperature sysertskite give the characteristic odour of osmium, but nevyanskite is not decomposed. Decomposition can be effected by fusion with nitre, the product being soluble in water. The mineral is found sparingly in certain platinum and gold washings, especially in those on rivers draining regions of peridotite and serpentine rocks. Its occurrence in situ has been recorded from Nizhni-Tagilsk in the Urals and at Bald Hill in Tasmania. Localities are in the Urals, Siberia, and Caucasus, particularly in Govt. Perm, *e.g.* at Nevjansk and Sysertsk (on Russian localities, *see* V. I. Vernadsky's descriptive mineralogy, vol. 1, St. Petersburg, 1908-1914; translation, in part, in Mining Jour. London, 1912, 98, 851); Japan, Borneo, New South Wales, Victoria, Tasmania, New Zealand, British Columbia, Quebec, Oregon, and northern California (here rather abundantly in the auriferous beach sands), San Domingo in the West Indies, Colombia, and Brazil. In South Africa it has been detected in the heavy concentrates from the auriferous banket of the Witwatersrand. The most profitable occurrence is that in the Savage river and other tributary streams of the Pieman river in north-west Tasmania, which rise in the district of Bald Hill where peridotites (harzburgite) and pyroxenites (enstatite-rock) with secondary serpentine rocks are exposed. In this material osmium predominates and very little platinum is present; analysis gave: Ir and Rh 33·80, Pt 0·37, Ru 8·19, Pd 0·21, Au 0·04, Fe 0·30, Cu trace, Os (diff.) 57·09 = 100 p.c. sp.gr. 18·87 and 19·5.

On account of its hardness and resistance to corrosion, the mineral is used directly for tipping the gold nibs of reservoir-pens, for surgical needles, watch pivots, and compass bearings. Selected grains free from flakiness are soldered with silver on the gold nibs, which are then split by a rotating metal disc charged with diamond powder, and finally ground down to shape. Other material is used for hardening platinum (for use as standard weights, jewellery, &c.), and as a source of iridium and osmium.

References.—J. F. Kemp, The geological relations and distribution of platinum and associated metals, Bull. U.S. Geol. Survey, 1902, No. 193; W. H. Twelvetrees, The Bald Hill osmiridium field, Bull. Geol. Survey Tasmania, 1914, No. 17. Several (15) analyses of iridosmine from Borneo are given by G. P. Chernik, Trav. Geol. Mus. Acad. Sci. St. Petersburg, 1912, 6, 49. L. J. S.

IRIS BLUE *v.* OXAZINE COLOURING MATTERS.

IRIS GREEN. *Sap Green* (*v.* PIGMENTS).

IRISH MOSS GUM *v.* GUMS.

IRON. Sym. Fe. At wt. 55·84. *History.*—Iron has been known and prized from the very earliest historical period, articles of the metal having been found among the contents of the Great Pyramid of Egypt, where they are believed to have remained for 5000 years. Iron was also used in Nineveh in considerable quantities, and in the British Museum are picks, hammers, and saws made of iron, found by Layard in the ruins of Nineveh, and which are believed to be of a date not later than 880 B.C. Iron is frequently mentioned in the earlier books of the Bible; it was much prized by the Greeks, and was discovered by Schliemann in the ruins of Mycenæ, which was destroyed B.C. 561. The Chinese were acquainted with the use of iron at a very early period, and it was also highly valued and much worked by the Romans. The metal employed in all the above instances was obtained by direct reduction from the ore, by methods very closely resembling those still in use by semi-barbarous peoples in various parts of the world. In England iron was largely worked by the Romans, and in the Forest of Dean there are still to be seen remains of these old Roman workings, whilst the partly reduced slags left by the Romans were in more modern times employed for many years in the blast furnaces of that district as a source of iron. At the Norman invasion Gloucester possessed a considerable trade in iron, but until the introduction of coal Sussex was the chief seat of the manufacture in this country. The exact date at which the blast furnace was introduced is not known, and it was probably the result of a gradual development of the more primitive hearths formerly in use. Cast iron was, however, known to Agricola, who died in 1555, and it was employed for cannon in this country in the year 1516. At this period small blast furnaces were employed which were capable of producing about 7–10 tons of metal per week, the fuel used being charcoal. The resulting pig iron was afterwards converted into wrought iron in a finery, or small hearth, not unlike the smith's fire. The large quantities of wood employed for the production of charcoal for this manufacture led to the introduction of various Acts of Parliament during the 16th century, which had for their object the restriction of the industry to certain districts, and a diminution of the waste of valuable timber. In the early part of the 17th century Dud Dudley succeeded in 'charring' coal or producing a coke suitable for use in the blast furnace, but the use of coal did not become general until after Abraham Darby had again succeeded in the manufacture of coke at Colebrook Dale about 1730. The introduction of the steam engine by Watt led to the use of more powerful blowing machinery, and gave increased yields, which again were much improved upon by the application of hot blast in 1829, by subsequent alteration in the shape of the interior, and by the considerable increase in the size and the capacity of the furnaces. Various other improvements have from time to time been adopted, such as improved methods of calcining the ore, and of charging the materials into the furnace; and the utilisation of the gases from the furnace for heating the blast, and for the blowing engines, so that the present output of the best furnaces is about 400 times that of the blast furnaces of 200 years ago, whilst the consumption of fuel has been reduced to about one-fifth of that formerly employed. In connection with the manufacture of steel, the cementation process is in various forms of very great antiquity, but a notable improvement was effected by Huntsman, about 1740, by the introduction of cast steel, while a further advance was made in 1839, when Heath introduced the use of manganese in steel melting. Wrought iron, as before mentioned, was originally prepared directly from the ore, and at a subsequent date was obtained from cast iron by the use of the open-hearth finery. In 1784 Cort patented the puddling process, and in so doing laid the foundation of much of the prosperity of England during the century that followed. But in recent years the whole system of the manufacture of wrought iron has been revolutionised by the magnificent inventions of Bessemer and Siemens, by which the decarburised iron is obtained in the fluid condition. The metal then is commonly known as 'mild steel,' and has met with such a variety of applications that for rails, girders, guns, shipbuilding, bridge construction, and many other uses, it has gradually replaced the iron obtained by the puddling process.

Of later inventions reference may be made to the introduction of the basic process, by Thomas, which rendered phosphatic ores available for steel making; the production of manganese steel by Hadfield thus laying the foundation of the important series of alloy steels; and the invention of the continuous process of steel making by Talbot.

Chief iron ores. Iron is occasionally found native, either in the form of meteorites also containing nickel, or as metal which, by the action of heat and reducing agents, has been naturally separated from the ore. These sources are, however, unimportant, except for savage tribes, who are in some instances largely dependent upon such methods of supply. Iron is very widely distributed throughout the crust of the earth in various forms. On account of its cheapness, and the readiness with which it combines with various elements, such as sulphur, phosphorus, or arsenic, which, if present in the metal, would injuriously affect its mechanical properties, comparatively few ferruginous compounds are practically available as sources of iron. It is necessary if an iron ore is to be profitably employed that the working expenses and carriage should be small, that the ore should be rich and readily reduced, and that it should be free from sulphur, phosphorus, arsenic, or other impurities which seriously deteriorate the quality of the iron. Such ores are practically either oxides or carbonates.

Oxides of iron. These may be divided into three classes.

1. *Magnetites.* Magnetic oxide of iron (Fe_3O_4) is the richest oxide of iron which occurs in nature; if pure, it would contain 72·4 p.c. of metallic iron. Its colour varies from brownish-grey to iron-black; it is brittle, magnetic, and produces a black streak. It crystallises in the cubic system, but is generally found massive. It occurs in remarkable purity in Sweden, also in India, and in immense quantities in the region of Lake Superior. The Swedish iron, which has so long been famed, is made from this ore. *Ilmenite* is an impure magnetite containing titanium, which occurs in Norway. *Franklinite*, which occurs in New Jersey, may be regarded as a magnetite in which the ferrous oxide is more or less replaced by oxide of zinc; and *Chrome Iron Ore* is a magnetite in which the ferric oxide is replaced by oxide of chromium. Magnetic iron sands occur on the shores of Java and New Zealand.

2. *Red hæmatites.* Ferric oxide (Fe_2O_3) occurs in a number of forms which possess different physical characters, such as *Micaceous iron ore*, *Specular iron ore*, *Kidney iron stone*, &c. These forms differ in hardness, density, and colour, but gives each a red streak. Red hæmatite is generally very free from phosphorus, and is found in Cumberland, where it is employed in the preparation of a pig iron low in phosphorus, suitable for the ordinary, or, acid, steel making process. Many of the ores of Spain and of the Lake Superior district, such as those of Vermilion, are red hæmatites. Hematites are also obtained from Algiers, and from Cuba, while very large deposits occur in Brazil. These are all low in phosphorus.

In the United States a deposit of phosphoric red fossil (hæmatite) ore runs from Clinton in the State of New York to Birmingham in Alabama.

3. *Brown hæmatites* Ferric oxide occurs associated with a variable amount of combined water in the different varieties of brown hæmatites. In colour these vary from light to dark brown and they give a brown streak. A specially rich, pure, and easily reducible variety is now imported in large quantities from Spain, and a pure variety was formerly worked in the Forest of Dean. In Northamptonshire and Oxfordshire, a brown hæmatite is employed which contains about 10 p.c. of silica and over 0·5 p.c. of phosphorus. In Lincolnshire large deposits of a similar character occur, but the silica is replaced by calcium carbonate. The *minette* ores of

France and Lorraine, in the vicinity of the Rhine, although phosphoric, and containing only about 30 p.c. of iron, are of this class, and are among the most important iron ore deposits of the world. Brown ores are also met with in considerable quantities in the United States. *Limonite*, *Bog iron ores*, and *Lake ores* are other examples of hydrated oxides of iron occurring in various localities. *Laterite* is found in India and other tropical countries. It is formed by a curious replacement of silica by hydrated oxide of iron. It is usually poor in iron, but in some localities is rich and important.

Carbonates. These consist essentially of ferrous carbonate ($FeCO_3$), the notable differences in character observed in various ores depending chiefly upon the amount and character of the impurities present. These ores are widely distributed and of great importance.

Spathic iron ore is the purest form in which ferrous carbonate occurs; it has a pearly lustre, and is generally light brown in colour. There are very extensive deposits of this ore in various parts of Europe, notably at Erzberg in Styria; the ore is usually free from phosphorus, but contains much manganese.

Clay iron stone is a less pure variety of ferrous carbonate which contains clayey matter, and was for many years the most important ore of this country; it usually occurs in the coal measures. The ore is generally dark in colour, and contains from 30 to 40 p.c. of metallic iron, associated with less manganese and more phosphorus than in the purer spathic ores.

Cleveland iron stone is a variety of clay iron stone met with in the North Riding of Yorkshire. It is generally uniform in character and contains about 30 p.c. of metallic iron; it contains little manganese, but the percentage of phosphorus is higher than in any of the ores previously mentioned, except, perhaps, in the case of the impure brown hæmatites.

Black band iron stone is an ore which occurs chiefly in Scotland and North Staffordshire. It contains a variable amount of bituminous matter which imparts a characteristic black colour, and which frequently enables the ore to be calcined without the addition of any extra fuel. In other respects black band very closely resembles clay iron stone.

In addition to the ores previously enumerated, several other materials are employed for the production of iron, such as 'tap-cinder,' which is essentially ferrous silicate, and is produced in the puddling process. It was formerly used for making a cheap phosphoric iron known as 'cinder pig,' but is now in demand for basic pig iron for steel making. Tap-cinder is only met with in quantities suitable for the requirements of blast furnaces in those districts where puddling has been conducted for a considerable period. 'Flue cinder' is a richer and purer silicate of iron obtained from furnaces in which iron or steel is reheated previous to rolling. The residue from Spanish pyrites, after the extraction of sulphur and copper, is commonly known as 'purple ore,' and has been made into bricks and used in the blast furnace. It is often used as a fettling in the puddling process.

The following table will illustrate the approximate composition of the various ores of iron. It will be understood, of course, that such materials are subject to considerable variations in character, and it has been thought better to give approximate values deduced from a number of analyses, than to introduce a mass of figures detailing actual results obtained.

APPROXIMATE COMPOSITION OF IRON ORES.

—	Magnetite	Red hæmatite	Brown hæmatite		Carbonate ores			
			Lake Superior ore (Mesabi)	Northampton	Spathic	Clay band	Cleveland	Black band
Ferric oxide (Fe_2O_3)	65	90	85	65	—	0·5	3	3
Ferrous oxide (FeO)	25	—		—	50	47	40	41
Manganous oxide (MnO)	—	—	—	0·5	10	2	1	1
Carbon dioxide (CO_2)	—	—	—	—	38	30	25	26
Silica (SiO_2)	10	6	6	13	2	10	8	7
Alumina (Al_2O_3)	—	1	2·5	3	—	5	7	3
Lime (CaO)	—	1	0·75	variable	—	2	7	2
Magnesia (MgO)	—	—	0·5	—	—	2	4	1
Phosphorus pentoxide (P_2O_5)	trace	trace	0·22	1·3	trace	0·6	1·5	0·6
Water	—	—	5	14	—	1	2	1
Organic matter	—	—	—	—	—	trace	trace	15

A full account of the occurrence, properties, and supplies of the chief iron ores of the world has been prepared by the Imperial Mineral Resources Bureau, and is now in course of publication (1921).

Preparation of iron ores.—The greater part of the iron ores now raised are charged into the blast furnace without any special preparation. Anhydrous oxides, such as Lake Superior ores, do not require calcination, except in some cases, to remove sulphur. The chief European ores are, however, treated before smelting. The mechanical preparation of iron ores is very simple, and consists of a rough assortment of the size of the materials to be employed. In some cases the larger pieces are broken by hand or suitable crushing machinery, whilst in other instances the very fine ore is separated by riddles, and briquetted, or sintered, or used for other purposes, as it would be apt to choke up the blast furnace. Poor ores, such as those of Cleveland, are charged in larger pieces than the richer hæmatites or magnetites. Non-calcareous ores, which contain iron pyrites, are frequently weathered for a few months, and the sulphur, becoming oxidised, passes away in solution as ferrous sulphate. Shale is also removed by weathering.

Magnetic Concentration is employed for the separation of gangue, pyrites, or calcium phosphate. The magnetic ore, such as that from Scandinavia, is crushed and passed either when dry on a revolving drum or belt in front of powerful electro-magnets; or the crushed ore is mixed with water and caused to flow in front of the magnets. In other cases the finely crushed dry ore is allowed to fall past terminals charged with electricity of high potential. The richer and purer particles become charged differently from the gangue, and may be deflected into separate bins. Ores which are not originally magnetic often become so on roasting, and may be successfully treated provided that the impurities are mechanically separable and not intimately mixed.

Calcination.—Many iron ores are calcined before being used in the blast furnace, the object being to remove volatile substances such as sulphur, water, carbon dioxide, arsenic, &c., and to concentrate the iron in the residue. Two other important objects are also gained by calcination; in the first place the iron is oxidised from the ferrous to the ferric condition, which prevents the formation of scouring slags, rich in ferrous silicate, during reduction in the blast furnace; and further, the material is rendered much more porous so that it is more readily acted upon by the gases of the furnace. From the above remarks it will be evident that some ores, such as red hæmatites, do not require calcination. Ores which are in a state of fine division, such as much of the ore from the Lake Superior district, are not calcined. Fine ores are frequently briquetted, and the briquettes are generally calcined before use in the blast furnace. When calcining, it is necessary to regulate the temperature as carefully as possible; with low temperatures the ore is insufficiently calcined, whilst if the heat be too great, or too much fuel is employed, the materials clot together and much of the benefit otherwise obtained is thus lost. Calcination is often conducted in open heaps, or between rectangular walls, exactly as in the case of many ores of other metals; but these methods are costly in fuel, space, and labour, and are apt to give irregular results, so are chiefly used for roasting tap-cinder in Staffordshire, or the black bands of North Staffordshire and Scotland, in which latter case the ore itself contains the necessary fuel. Kilns are now very generally employed for calcining, and in the Cleveland district the use of large circular kilns, constructed of iron lined with fire brick, is almost universal. In such kilns the ore and fuel are charged in at the top, and the calcined material removed from the bottom, the operation being continuous; in such kilns calcination is well under control, fuel is economised, and labour is saved. Rectangular kilns, fired with surplus gas from the blast furnace, have been introduced both in the United Kingdom and elsewhere.

Production of pig iron.—The ore, having if necessary been prepared as before described, is now *smelted* in the *blast furnace* to produce pig iron. For this purpose it is introduced at the top of the furnace together with the *flux* necessary to form a fluid slag (or 'cinder') with the gangue of the ore; *fuel* is also added in sufficient quantity to melt the materials and to reduce the iron. The air necessary for combustion is introduced near the bottom of the furnace, having been blown, and usually also heated, by suitable appliances. The operation is continuous, a furnace frequently working without any important stoppage for a number of years. The whole of the materials introduced into the furnace have either to be melted and flow off from the bottom as iron and cinder, or to be converted into vapour and pass off as 'waste gases' from the top.

The blast furnace.—The earliest type of blast furnace is shown in Fig. 1, which represents a form employed on the Continent for the production of wrought iron about 500 years ago. After the furnace had been heated, ore and fuel were introduced at the top, and blast from below; the result was the production of a bloom of wrought iron, which, owing to the low temperatures of such furnaces, was never melted, but was removed by taking down the brickwork at the front of the furnace. Doubtless in some of the larger furnaces of this description cast iron would sometimes be accidentally obtained, and as the value of this material for castings, and for the direct production of wrought iron by means of the finery came to be recognised, cast iron would be regularly made. This change was probably introduced early in the 16th century, and the furnaces gradually increased in size until they were capable of producing about 20 tons of pig iron per week, using charcoal for fuel. About two centuries ago coke was introduced as fuel in the blast furnace, and the size and production were slightly increased. Since this period enormous changes have been introduced, commencing with the use of coke about 1735; of hot blast in Scotland in 1829; the adoption of round and larger hearths in South Staffordshire about 1835; the utilisation of

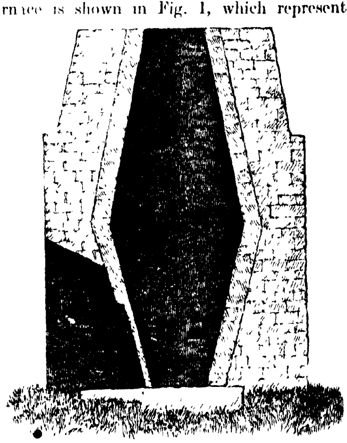


FIG. 1.

the waste gases; the largely increased height and capacity adopted in the Cleveland district shortly after 1860, and the use of hot blast stoves on the regenerative principle. A remarkable development took place in West Pennsylvania about 1890, and as a result of easily reducible ores, smaller and steeper furnaces, higher blast pressure, and increased engine power, a weekly production of nearly 5000 tons of pig iron per furnace has been attained. Fig. 2 represents a Cleveland blast furnace, the height of which would be about 80 feet, its capacity about 25,500 cub. ft., and the weekly production of pig iron varying from 500 to about 1000 tons, according to the character of the ore used, the temperature and pressure of the blast, and other circumstances. Such a furnace is closed at the top by means of the 'cup and cone' arrangement, into which the materials are charged, and delivered into the furnace at suitable intervals by lowering the moveable cone. The combustible gases are conducted by means of suitable pipes to the regenerative stoves employed for heating the blast, or to the boilers required for raising steam for the works. A portion of the gases is carefully cleaned from dust and used for power purposes in gas engines. The dust recovered from the cleaning of the gases is rich in potash salts, and has become an important source of potash in the United Kingdom. The furnace itself is very light in construction for so large an erection, which is intended to contain a great weight and to resist a very high temperature. The outer casing is of iron plates riveted together, and the furnace is lined with refractory firebrick. The blast is delivered into the furnace by about six twyers, which are connected with the hot blast main, and which are water-jacketed where they enter the furnace to prevent them being rapidly destroyed by the high temperature. The following summary will illustrate the nature of the products, and the approximate weight of the charges employed for the production of 1 ton of No. 3 Ormesby (Cleveland) hot blast pig iron:

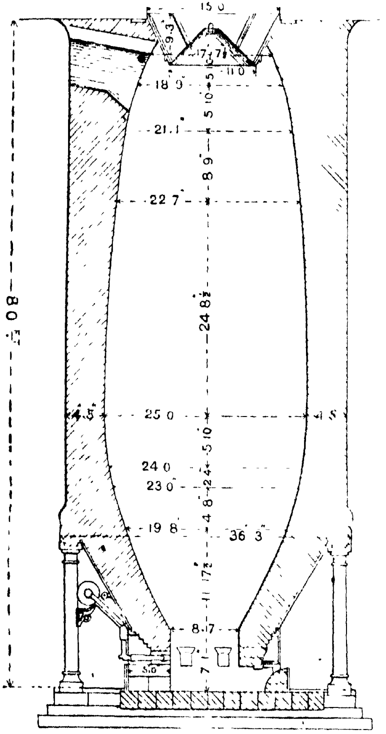


Fig. 2.

Charge	cwt	Products	cwt.
Calcined iron stone	48	Iron . . .	20
Limestone . .	12	Slag . . .	30
Hard Durham coke	20		
Blast . .	100	Waste gases .	130
	9 tons		9 tons

In working richer ores, such as hæmatites, the amount of limestone and ore employed would be less than the quantities required in the Cleveland district, and the weight of slag would be proportionately diminished. To prepare a No. 1 pig iron the quantity of fuel used would be somewhat greater, whilst with a No. 4, or a white iron, rather less fuel would be required; the weight of the blast and of the waste gases would vary correspondingly. Usually the only material added as a flux is limestone, which is sometimes burnt before being charged into the furnace. Other fluxes are often indirectly added in the form of iron ores rich in argillaceous or aluminous matter, as mixtures of ore are frequently made to obtain a more fusible cinder. The fuel most generally used is hard coke, free from sulphur, and with as little ash as possible. Raw bituminous coal is used in Scotland and North Staffordshire and in parts of the United States, though lower furnaces are necessary as the fuel is more friable. Mixtures of coal and coke are not uncommon, and anthracite is employed in Eastern Pennyslvania. Charcoal is still used on the Continent in Sweden and in some parts of America (particularly Michigan) for the production of a superior class of iron where coal is scarce.

Any moisture which is present in the blast is decomposed in the furnace hearth, with the formation of hydrogen and carbon monoxide, and absorption of heat. Hence blast furnaces work better and more economically in cold dry weather. Gayley has successfully introduced a method of drying the blast, by refrigeration, before it is passed into the hot blast stoves. With large installations this leads to greater regularity of composition, increased output, and lower fuel consumption.

The chief changes which take place in the blast furnace may be briefly summarised as follows. The ore in the first part of its descent is rapidly heated to low redness, at which temperature the carbon monoxide, which at this point forms about 36 p.c. of the furnace gases, reduces the ferric oxide to metallic iron; thus

$$Fe_2O_3+3CO=Fe_2+3CO_2$$

The iron is not melted at this low temperature, but remains, as a metallic sponge, which if brought in contact with the air would rapidly burn, and so reproduce ferric oxide. At a part of the furnace slightly lower than that at which reduction is chiefly accomplished the limestone is decomposed, carbon dioxide being evolved and lime produced; thus $CaCO_3 = CaO + CO_2$. During the next stage of the process, which occupies more time than either of the others, the materials gradually descend to the boshes of the furnace, and in so doing absorb heat from the ascending gases. Carbon in a state of minute subdivision produced by the reduction of carbon monoxide, is also deposited in the pores of the spongy iron, which becomes more and more carburised as it descends to the hotter parts of the furnace where fusion takes place. In passing from the boshes to the hearth the temperature is sufficiently high to cause the combination of the silica in the gangue with the lime, alumina, and other bases in the charge, and thus to form a fluid cinder, which separates from the now molten iron, the latter sinking to the bottom of the hearth, while the slag, on account of its relative lightness, floats on the top. The cinder is either tapped off at intervals, or is allowed to flow regularly off through what is known as the 'slagging hole.' The iron is allowed to accumulate, and is then tapped off from a lower point, usually at intervals of about 12 hours, into moulds roughly made in sand. The product is cast iron, but on account of its being cast in long pieces of D section, which are called 'pigs,' and which generally weigh about 1 cwt. each, this variety of cast iron is commercially known as pig iron.

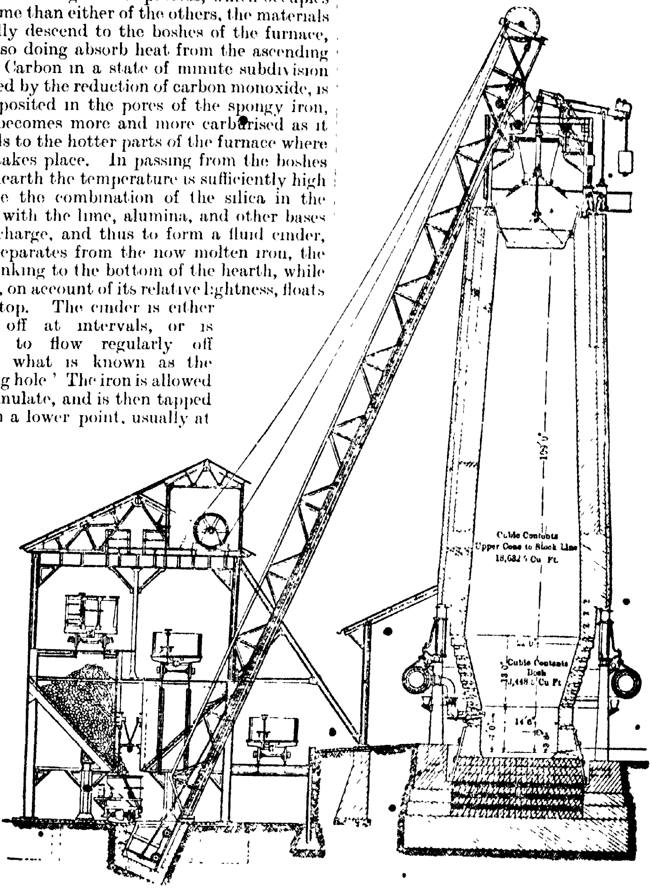


FIG. 3.—MODERN AMERICAN BLAST FURNACE WITH MECHANICAL CHARGING.

For steel making the iron is usually tapped off more frequently, and conveyed while still fluid, in ladles holding, say, 20 tons of metal, to the steel works.

Shaft furnaces are also employed for producing cast iron by heating with the electric current, in countries such as Sweden, where electric energy is cheap. The reduction is accomplished by means of charcoal, and the fuel consumption is only about one-fourth of that required in the coke blast furnace. This branch of the iron industry is as yet conducted only on a relatively small scale, but considerable progress has already been made. The gases from such furnaces are small in volume, and of low calorific value.

CHEMICAL PROPERTIES OF CAST IRON.

The metal obtained as just described is by no means pure metallic iron, but usually contains at least 5 p.c. of other materials, such as carbon, silicon, sulphur, phosphorus, manganese, chromium, &c., &c. The element which imparts the characteristic properties to cast iron is *carbon*, which is present to the extent of at least 1·5 p.c. Under ordinary conditions the maximum amount of carbon found in pig iron is 4·25 p.c., but in the presence of much manganese this amount may be considerably exceeded. The carbon is present in cast iron in two distinct conditions, known respectively as 'graphitic' and 'combined.'

Iron and carbon unite to form a definite carbide Fe_3C, and it is probable that in molten cast iron the carbon exists in solution in this form. This carbide is retained in solution if the metal is rapidly cooled, but on slow cooling, or conversely by long heating to a temperature of 900°, the carbide decomposes into the more stable condition of iron and graphite. Silicon assists the decomposition of the carbide. The graphite is of two kinds, primary and secondary. Primary graphite is formed at about 1050°, and occurs in relatively large flakes; it causes the iron to be soft and weak. Secondary graphite or 'temper carbon' is produced by decomposition of the residue of the carbide at a lower temperature (700°–800°). It is smaller, more evenly distributed, and the metal is soft but strong. The carbide may exist in solid cast iron in two forms, one of which separates at about 680° (the recalescence point), and can be seen by the microscope. The other is retained in solution at the ordinary temperature, and hence cannot be seen in micro-sections. The latter is sometimes called 'missing' carbon, as it is not determined in the ordinary Eggertz colour test.

Graphitic carbon renders the iron *grey* in fracture, soft to the tool, and capable of taking a sharp impression of a mould. Combined carbon gives a *white* fracture, the metal is very hard, it melts at a lower temperature, but is never so fluid as in the case of grey iron. Graphitic carbon may be separated from the metal either by mechanical or chemical processes, and may be obtained in either of these ways in a state of great purity. Combined carbon, on the other hand, cannot be mechanically separated from cast iron; whilst if white iron be treated with an acid, such as hydrochloric or sulphuric, the carbon passes off in the gaseous condition, with the hydrogen evolved, in the form of badly smelling hydrocarbons. The graphitic carbon, on the other hand, would in a similar case be left behind in the insoluble residue. Iron which contains combined and graphitic carbon in nearly equal proportions has a characteristic fracture, and on this account is called 'mottled' iron. Slow cooling produces grey iron, while rapid cooling, or 'chilling,' produces white iron.

Silicon is always present in cast iron, the amount varying from about 0·2 p.c. in specially pure Swedish iron, to upwards of 18 p.c. in some varieties of 'silicon pig,' which are specially prepared for certain purposes. Still richer 'ferro-silicons,' containing up to 50 or even 90 p.c. of silicon, are prepared in the electric furnace. In ordinary pig iron the usual limits are from about 1 to 4 p.c. The melting-point of pure iron (*circa* 1515°) is reduced to 1445° when the silicon content is 1·5 p.c. As the silicon content is measured the m.p is raised to 1516° (3 p.c. Si) and then falls again to 1410° (6 p.c. Si). A 7 p.c. Si alloy melts at 1427° and the fusion point falls regularly to 1256° (14·3 p.c. Si). When present in large proportions silicon renders the pig hard, weak, and brittle; it is also quite unsuitable for use in the puddling furnace on account of the waste of time and the injury to the lining of the furnace. Silicon, however, renders cast iron soft, strong, and grey when present in suitable proportions; and silicious irons have been largely used in the foundry on this account, as they allow of the use of larger quantities of foundry scrap, which is white and hard. They also allow in many cases of the employment of cheaper irons in foundry mixtures (Turner Chem. Soc. Trans. 1885, 577, 902; 1886, 130). For such purposes the amount of silicon should vary from about 0·8 to 3·5 p.c., according to the size and character of the work; the lower value would be employed for chilled rolls or other purposes where crushing strength is desired, whilst the higher value would be preferred where fluidity and softness are necessary. With higher silicon acid-resisting alloys are obtained. Usually between 15 and 20 p.c. of silicon is added for this purpose. With more silicon the alloy is less fusible, and more difficult to cast. In the blast furnace high temperatures and silicious slags favour the absorption of silicon.

Sulphur is generally present only in very small quantities in good cast iron. With much sulphur the metal is white, hard, and unsound in the foundry; and if converted into wrought iron or steel the product is red-short, and useless. In the blast furnace hot working, a slag rich in lime, and the presence of either silicon or manganese in the metal, prevents the absorption of sulphur.

Manganese is always present in pig iron; its reduction is favoured by hot working and basic slags. *Spiegel-eisen* is a white iron, containing upwards of 5 p.c. of manganese. With 20 p.c. of manganese or upwards, the metal is known as *ferro-manganese*; it frequently contains as much as 86 p.c. of metallic manganese. Both spiegel eisen and ferro-manganese are used in steel making, as additions at the end of the operation, the object being to add a little manganese to the bath of metal to prevent red-shortness.

Pig iron, which contains manganese, is generally low in sulphur; this fact has been applied to the production of a special pig for use in the basic process, where both sulphur and silicon are required to be present in small quantity.

Sulphur is removed from fluid cast iron for steel making by the use of 'metal mixers,' which are large vessels or furnaces capable of holding about 250 tons of fluid metal. If the iron does not already contain sufficient manganese that element is added, and manganese sulphide separates and passes into the slag. The desulphurised metal is drawn off as required and fresh iron added, so that the process is simple and continuous. Metal mixers also equalise the content of silicon, and this element may be considerably reduced in quantity by adding oxides of iron to the mixer slag.

Phosphorus varies from 0·02 in best Swedish or hæmatite iron to upwards of 3 p.c. in common cinder pig. In the case of each of the elements previously considered only a portion of that which is present in the blast furnace charge passes into the metal, but with phosphorus practically the whole of that which is present in the materials used passes into the pig iron, For foundry and forge purposes probably a little phosphorus is actually beneficial in cast iron; but in the case of wrought iron or steel its presence is highly prejudicial, as it produces remarkable brittleness in the metal when cold. Hence in the manufacture by the ordinary or 'acid' process, of either Bessemer or Siemens steel, only such pig iron as is free from phosphorus may be employed, since by the acid process no phosphorus is removed. For irons containing phosphorus the 'basic' process must be employed if they are to be converted into steel (*v. infra*, p. 673). A selection of representative analyses of cast iron will be found in Tables at the end of this article.

Grades of pig iron.—For a great number of uses pig iron is sold by the appearance on fracture. A pig which is very grey, with large crystals, is called No. 1; if the fracture shows smaller crystals it is called No. 2; with still closer grain it would be sold as No. 3 or 4. If white and grey are mixed it is called mottled; when graphitic carbon almost entirely disappears it is called white. On account of their softness and fluidity Nos. 1, 2, and 3 are chiefly employed for foundry purposes, and usually command a somewhat higher price. No. 4 is largely used in the puddling process, and would be called a forge or 'strong' iron. No. 4 is also employed in mixtures in the foundry when heavy castings are required, or when the metal is to be chilled —*i.e.* when the surface is to be rendered white and hard by cooling in contact with a mass of metal, technically known as a 'chill.' Mottled and white irons are chiefly used in mixtures of pig iron to give hardness, strength, or density.

Foundry practice.—The ironfounder commonly employs a mixture of irons, and it is the custom to mix not merely different grades of iron, but also metal from different localities. This originated at first from the results of practical experience, but it has since been shown in many cases to be in accordance with scientific knowledge, as the best foundry iron for any particular purpose contains a certain proportion of combined and graphitic carbon, silicon, phosphorus, &c. (Turner, Journ. Iron and Steel Inst. 1886), and these constituents can usually be best regulated by mixing together the irons obtained from different localities. If special strength is required the silicon should not exceed about 2 p.c., and the phosphorus should be somewhat less than half that quantity. But if softness and fluidity are specially desired, these amounts may frequently be nearly doubled without serious injury. The metal is melted in a small blast furnace called a cupola, which is constructed of iron plates, lined with firebrick or ganister; it is circular in section, and is driven with a low-pressure cold blast, introduced through twyers near the bottom. The metal is charged from the top, the fuel used being hard coke free from sulphur; the weight of coke varies from about 5 to 15 p.c. of the metal used, being higher with smaller outputs. A small quantity of limestone is added to act as a flux. The metal on melting runs down, accumulating in the bottom of the cupola below the twyers, and is then tapped off at intervals into suitable ladles. For special qualities of castings, melting is sometimes performed in a reverberatory furnace; this is more expensive, but gives a cleaner and more uniform metal, which can, if necessary, be tested before use. For the majority of purposes 'green sand moulding' is adopted, a pattern being first prepared and an impression obtained in fine sand, which has been previously mixed with a small proportion of carbonaceous matter, such as coke dust. For special work, or intricate forms, other varieties of moulds are prepared, which are often of loam; these are supported by masonry, and braced with tie rods, &c., as may be found necessary. Such moulds are carefully dried before being used; in some cases drying is performed in stoves at a low red heat, in other instances by means of a fire which is placed inside the mould. In the latter case gaseous fuel is commonly employed. Green sand moulds are not dried before use; where they can be employed they have the advantages of rapidity and economy.

Iron, when remelted in the foundry, becomes harder, owing to the elimination of silicon and the absorption of sulphur. Hence in some cases, when the metal is originally too soft, a great improvement is noticed on remelting several times; but in other cases no improvement is observed, and frequently deterioration results. Many observers, among them Sir W. Fairbairn (Brit. Assoc. Report, 1853, 87), have stated that iron is improved by remelting a certain number of times, and that afterwards by further melting it again deteriorates. But the experiments of various observers gave very conflicting results in this direction, some recommending very few meltings, others a larger number. It has been shown by Turner (Chem. Soc. Trans. 1886, 493) that the effect formerly attributed to the operation of remelting is really due to the chemical changes which take place during that operation, and that the chemical composition of the product, when rightly understood, gives an indication of its mechanical properties.

Production of wrought iron.—It has already been mentioned that by the earlier processes wrought iron was produced directly from the ore. Similar processes are still carried on by semi-civilised races in various parts of the world, and in an improved form direct reduction is still practised in parts of America where charcoal is cheap, and where no ready means of transit exist. Many attempts in the same direction have also been made in various parts of Europe. In several instances great expectations have been raised in connection with these suggested improvements, but none of them has met with much commercial success. In these methods of reducing the iron ore the temperature employed is usually not sufficiently high to melt the metal obtained; the phosphorus present in the ore remains in a great measure in the slag, which is rich in oxide of iron, and the wrought iron obtained even from moderately phosphoric ores, is still sufficiently pure to be useful. The direct method is usually extravagant both in fuel and labour, whilst the slags produced frequently contain sufficient iron to make them valuable for use in the blast furnace.

Wrought iron is now generally prepared by an indirect process, cast iron being produced as an intermediate product between the ore and the finished metal. The impurities of the crude pig iron are then removed by oxidation, and pass away either in the form of gas, as with carbon, or, like phosphorus, silicon, and manganese, remain in the slag. This purification was originally performed in small hearths called 'fineries,' and for the production of specially selected metal these have survived in isolated places to the present day. But a most important change was introduced in 1784, when Cort patented the puddling process, in which the operation of purification is conducted in a reverberatory furnace. In Cort's original furnace the working bottom was made of sand, and white pig iron was employed; the iron never became perfectly fluid, and from the pasty character of the metal the 'puddling' process derived its name. This original form of the process has now almost entirely given way to what is known as 'pig boiling,' in distinction from the earlier 'dry process.' Pig boiling was introduced by Joseph Hall, of Tipton, Staffordshire, about 1820. In principle the operation is exactly the same in either case; in practice the chief differences are in the construction of the furnace, the materials forming the bottom, and the kind of cast iron employed. In the more modern process (which, however, is gradually being replaced by the use of 'mild steel') the furnace bottom is constructed of cast-iron plates, and the bridge is internally cooled either by air or water; the cast-iron bottom plates are covered with a layer of oxide of iron about 3 inches thick, which forms the working bottom of the furnace; the sides are formed of fettling, also consisting essentially of oxide of iron; the metal used is a grey iron, usually what is known as a No. 4 forge quality. The result of these changes is that the furnace works with fewer repairs; that, owing to the use of oxidising fettling, the operation is conducted more rapidly, and larger charges can be employed; whilst, as grey iron is used, the metal is perfectly fluid when melted, and 'boils' vigorously during the elimination of the carbon. A sketch of the furnace is given in Fig. 4.

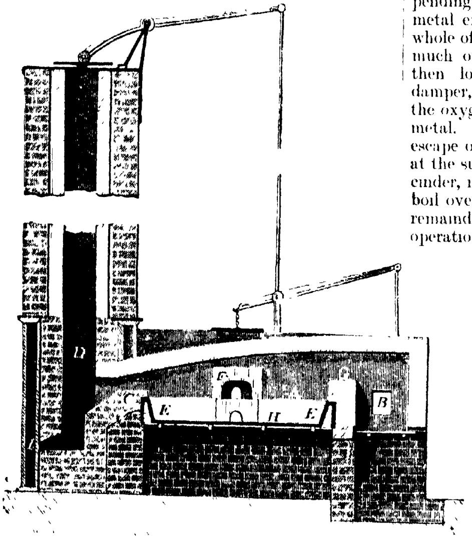


FIG. 4.—THE PUDDLING FURNACE.

A, Furnace bed; B, Firing hole, C, Flue, D, Chimney; E, Fettling, F, Working door; G, Fire bridge; H, Cast-iron bottom plate.

The operation is conducted as follows. The furnace being at a red heat from the previous charge, the fettling is repaired, as necessary, by the addition of 'bull-dog,' pottery mine, hæmatite, or other forms of oxide of iron. About 4 or 4½ cwts. of pig iron are then charged on to the bed of the furnace, the door being closed and the temperature raised while melting proceeds. After about 30 minutes the iron is generally melted, and is then kept fluid and well rabbled for about 10 minutes, the length of time depending very much on the composition of the metal employed. By this time practically the whole of the silicon will have been removed, and much of the manganese. The temperature is then lowered somewhat, by regulating the damper, and a violent reaction ensues between the oxygen of the fettling and the carbon in the metal. The iron boils vigorously owing to the escape of carbon monoxide, which burns in jets at the surface, and a quantity of slag, called tap cinder, is removed, part of this being allowed to boil over the fore plate of the furnace, and the remainder being tapped out at the end of the operation. The phosphorus gradually passes out during the process, being eliminated most rapidly at this stage, and passing into the tap cinder. After the boiling stage is over the metal 'drops' and 'comes to nature'—*i.e.* granules of malleable iron gradually separate, and the whole becomes quite pasty. In this condition it is 'balled up' by the puddler into blooms, each of which is somewhat under 100 lbs. in weight. These are then hammered and rolled, forming puddled bar,' which is not yet fit to be sent into commerce. The whole operation of puddling usually occupies about 70 minutes. Analyses of forge irons, puddled bar, &c., are given in Tables at the end of this article. The puddled bar is cut up into lengths and made into suitable bundles called 'piles,' which are reheated in a furnace, which is larger but otherwise very similar in construction to that in which the puddling operation is conducted. The piles are withdrawn at a welding heat, and hammered or rolled to produce merchant iron, best iron, best best iron, &c., according to the quality and the amount of work expended on the material. A number of attempts have been made to introduce mechanical contrivances to replace the laborious process of puddling; but, after numerous trials, these have been almost entirely abandoned in this country, though a revolving furnace invented by Danks was successfully used in America. Wrought iron was formerly used for ship building, bridge construction, rails, armour plates, and similar purposes, for which it has since been replaced by steel. Wrought iron is now chiefly employed for purposes which require a reliable metal which can be easily welded or otherwise worked by the smith. It is also used for tubes, wire, sheets, and fittings which are exposed to atmospheric oxidation.

Steel. Steel was formerly defined as a variety of iron which contained from 0·5 to 1·5 p.c. of carbon, and which was capable of being hardened and tempered. This definition however, has now to be extended so as to include various forms of 'mild steel' which contain under 0·5 p.c. of carbon, and which cannot be hardened. We therefore include under the designation of 'steel' all metal which, though containing under 0·5 p.c. of carbon, has been produced in the molten condition. In such a classification wrought iron is obviously excluded, as it is produced in a pasty form. The characters of steel depend largely on the proportion of carbon and other elements which enter into its composition. With low percentages of carbon the metal possesses great ductility, moderate tenacity, and very slight power of hardening. With 0·45 p.c. of carbon the ductility is somewhat less, the tenacity greater, whilst its hardening power is quite appreciable. Such a metal would be employed in the manufacture of rails and for similar purposes. With from 0·6 to 1 p.c. of carbon the ductility is still lower, whilst the tenacity reaches upwards of 40 tons per square inch of section, and a metal is obtained which can be readily hardened and tempered. This class of steel is largely used for cutting tools, drills, dies, &c., and for best purposes is still usually produced in crucibles. The use of the electric furnace is rapidly extending for the production of tool steels, especially for such as contain other elements in addition to carbon. With carbon from 1 to 1·5 p.c. a steel is obtained which is suitable for the hardest tools, and which requires to be very skilfully hardened and tempered. As the proportion of carbon increases the steel requires to be worked at a somewhat lower temperature. With upwards of 1·5 p.c. of carbon the metal is brittle, is no longer capable of being hardened, it is more fusible, and thus gradually passes into cast iron. Hardening increases the tenacity of steel, but diminishes its ductility. The tenacity of steel, like that of wrought iron, is also increased by the amount of work done in rolling or in drawing out the metal into wire, and certain varieties of steel wire are prepared which have a tensile strength of upwards of 150 tons per square inch. The presence of manganese in steel increases its tenacity; in suitable proportions it also very materially improves the working properties of the metal, and on this account is employed both in crucible steel making and in the Bessemer and Siemens processes. In large quantities manganese renders steel permanently harder, and also causes it to be unmagnetisable (Hadfield). 'Manganese steel' contains about 10 p.c. of manganese. It is permanently hard, and is used chiefly in the form of castings for tramway points, stamp batteries, and many similar purposes (*cf.* Hall, J. Soc. Chem. Ind. 1915, 57). Phosphorus renders steel cold-short, and should on this account not exceed 0·1 p.c., whilst crucible steel of special quality usually contains not more than 0·04 p.c. of phosphorus. Sulphur renders steel red-short, and should never exceed a few hundredths per cent. Silicon in the absence of any reducing agent forms silica, which renders mild steel red-short and brittle, although the presence of manganese very much modifies these effects, so that with about 0·5 p.c. of manganese several tenths per cent. of silicon may be present without injury. In steel castings about 0·3 p.c. of silicon is frequently added to promote soundness. A special steel, containing about 3·5 p.c. of silicon, is used for the production of sheet steel for armatures, as it shows remarkably low hysteresis losses. Arsenic renders steel both hot- and cold-short; practically the whole of the arsenic present in the blast furnace charge passes into the pig iron, and is not removed during conversion into steel (*v.* Stead, also Harbord and Tucker, Jour. Iron & Steel Inst. 1888, part 1). Chromium in small quantities gives increased tenacity, and on this account is frequently added to basic or other very mild steel so as to impart greater strength. With considerable proportions of chromium the welding power of steel is much reduced. Chromium is added to steel shells as the penetrating power is thereby greatly increased. It is also employed in the production of rustless or stainless steel for cutlery. Aluminium is frequently used for addition to fluid steel for deoxidising purposes. It assists in the production of solid ingots, and prevents segregation of the impurities. The amount of aluminium left in the steel is, however, so small as to be with difficulty estimated by analysis. Nickel is added to mild steel for shipbuilding and constructional purposes, usually to about the extent of 3·5 p.c., as it imparts increased tenacity with unusual ductility. With higher proportions of nickel hard non-magnetic alloys are obtained, which are only used for certain special purposes. Chrome-nickel steels, containing about 1 p.c. of chromium and 3·5 p.c. nickel, are used for tools and in automobile construction. In recent years tungsten has been used on a very considerable scale for the production of self-hardening and other 'special' steels. Usually about 6 or 7 p.c. of tungsten is added; the steels are made in crucibles, and contain from 1 to 2 p.c. of carbon. High-speed steels contain still more tungsten, and retain their cutting properties even at a red heat. Vanadium is also added to mild steels with marked advantage, a very small percentage giving improved physical properties. Much attention is now being devoted to the production of special alloy steels for a variety of purposes. They generally contain from 0·6 to 1 p.c. of carbon, with varying proportions of manganese, chromium, nickel, cobalt, tungsten, molybdenum, vanadium, &c. Such alloy steels are now generally melted in the electric furnace in charges varying from about 2 to 10 tons.

Manufacture of steel.—A variety of steel, or more correctly steely iron, was obtained by the earlier processes used for the production of wrought iron directly from the ore, when the process was modified by altering the amount of blast used, and the angle at which it was introduced, together with a slight increase in the quantity of fuel employed. By these means the metal prepared contained sufficient carbon to impart steely properties, although when obtained by such methods the steel is never of uniform quality. A steely iron was also frequently prepared in the puddling furnace when the process was carried on in such a manner as to remove the metal before the carbon was completely eliminated. But for some centuries at least the best varieties of steel have been prepared by what is known as the 'cementation' process. For this purpose, bar iron of the best quality is cut up in suitable lengths and placed in charcoal in the cementation furnace. This furnace consists essentially of two rectangular chambers which are constructed of firebrick, and are arranged to contain the iron and charcoal. The charge of iron used in one operation is generally about 15 tons. A fireplace under the chambers supplies the necessary heat, whilst the whole is contained in the base of a large conical chimney stack. The iron is carefully arranged and surrounded with charcoal, the rectangular chests, which are open at the top, being covered with 'swarf' to protect the contents, as far as possible, from oxidation. The heat is continued for about 7 days, although the time will vary somewhat with the temper required and other circumstances. The progress of the operation is judged by the appearance of the fracture of trial bars, which are removed and examined from time to time. The product is known as 'blister' steel, the name being derived from the characteristic appearance of the surface. Percy has shown that this is probably due to carbon monoxide evolved at a high temperature by the action of carbon on the oxygen of the intermingled slag. In good blister steel the protuberances should be as evenly distributed as possible. When fractured, the blister steel is generally found to consist of an outer crystalline layer of steel surrounding an inner portion of less altered iron. The exact theory of cementation has not been made out with certainty, although Roberts-Austen showed that pure iron became carburised when heated with a diamond *in vacuô*; but under usual conditions carbon monoxide is known to play an important part in the process. The result is that the metal, when heated in contact with solid carbon, becomes gradually carburised on the outside, and if the heating be continued for a sufficient length of time, carburisation gradually extends throughout the whole of the mass. Blister steel, when piled and reheated, is known as 'shear' steel, and gains considerably in uniformity by the treatment. The name is derived from the fact that shears used for cutting woollen cloth were formerly made of this variety of steel. But for best steel for tools and other purposes it is usual to employ 'cast steel,' the best qualities of which are prepared by melting blister steel in clay or plumbago crucibles. The charges usually weigh somewhat less than 100 lbs., a little glass or other flux is employed, and the crucible is kept covered while melting proceeds. Heating is conducted usually in wind furnaces, using coke as fuel, though gaseous fuel has also been employed. It is contended that gaseous fuel has the advantage of being more under control; it is also economical in working, and enables the process to be carried on continuously, whilst the wind furnace 'clinkers' up and has to be stopped for cleaning. Cast steel is also prepared in crucibles from materials other than blister steel, but the product is usually of an inferior character. It is found advantageous (especially with cheaper mixtures) to introduce a little manganese in the production of crucible steel, as the metal then possesses better working qualities. The 'body,' which is so characteristic of good steel, appears to be closely connected with its chemical composition, and is associated with special freedom from phosphorus and similar impurities. Crucible steel contains a few hundredths per cent. of silicon, which is reduced from the silicious material of the crucible during the melting, and which appears to play an important part in producing solid castings. For special purposes, in recent years, considerable quantities of manganese, nickel, chromium, tungsten, and of other elements have been added to steel produced in the crucible, and the 'special' steel industry has become important both in this country and abroad. But, as before stated, the electric furnace has been introduced on a very considerable scale, for the production of such special steels.

Bessemer steel. The method of producing steel with which the name of Bessemer will always be connected, and which has done so much to revolutionise the iron trade of the world, was described and patented in 1856. At first great incredulity was manifested by ironmasters, and the product was inferior; but when it came to be recognised that only iron free from phosphorus could be employed in this process, and that the red-shortness which at first had been so difficult to overcome could be removed by the addition of manganese before tapping the metal, the success of the process was assured. The iron now used in the ordinary, or as it has come to be called the 'acid' Bessemer process, is of special quality, and is made from ores of hæmatite quality. It should contain only a few hundredths p.c. of phosphorus, and about 1–3 p.c. of silicon. With rapid working, as in the large American works, the silicon is about 1 p.c. lower than is the custom where fewer charges are run in the same time as in England. The metal is either remelted in a cupola or is run in the fluid state from the blast furnace, or the metal mixer, according to circumstances, but in any case is introduced in the molten condition into an egg-shaped vessel known as a 'converter,' and which has been heated either by a previous charge or by lighting a fire inside. The converter is constructed externally of iron plates, and is arranged so as to rotate on trunnions which are fixed on either side a little below the middle of the vessel. By this arrangement the converter can be readily manipulated as required during the process. At the lower part of the vessel is a moveable bottom, fitted with a blast box into which air is admitted during the 'blow' at a pressure of about 20 lbs. to the square inch. From the blast box the air enters the vessel through a number of holes passing through a fireclay or ganister bottom lining. The sides of the converter are generally lined by means of ganister (a silicious or 'acid' material) which is generally rammed into position. At the top of the converter, a little on one side, is an opening which serves for the introduction of the metal in the first place, then for the escape of waste gases during the blow, and lastly for the tapping of the metal and slag when the operation is concluded. The charge of pig iron, which weighs from about 8 to 12 tons, is introduced while the vessel is in a horizontal position, in order to avoid closing the twyers at the bottom; the blast is then turned on and the vessel rotated so as to cause the blast to rise through the bath of metal. The silicon present is rapidly oxidised and passes into the slag, at the same time producing sufficient heat, not merely to maintain the fluidity of the metal, but actually to very much increase its temperature. After the silicon has in this manner been removed, which generally occupies about 10 minutes, the carbon is attacked, and this is rendered evident by a marked increase in the size and luminosity of the flame produced. This flame continues for rather more than 10 minutes, and then, when the carbon has been burned out, suddenly 'drops,' *i.e.* becomes much smaller and less luminous, showing that the operation is concluded. During the whole of the blow the metal remains molten, and the temperature produced by the combustion of the carbon and silicon is so great that the resulting decarburised metal can be readily poured into suitable ingot moulds. But if used in this form, when it is almost perfectly freed from carbon and manganese, the metal would be red-short, and would also be too soft for many purposes. It is usual, therefore, after the flame has dropped, to add a quantity of spiegeleisen or ferro-manganese in order to counteract this red-shortness and to introduce the required amount of carbon. After the requisite addition has been made the metal is allowed to stand a few minutes so as to some extent to mix the constituents; it is then 'teemed' into the ladle and thence cast into ingots.

The basic Bessemer process.—It will be noticed that in the original Bessemer process the vessel is lined with silicious or acid materials, and only cast iron free from phosphorus can be employed, as practically none of this element is removed during the blow. But a modification of the process was introduced by Messrs. Thomas and Gilchrist, which most successfully solved the problem of the treatment of phosphoric iron. Fig. 5 (after A. Holley) shows the general arrangement of a basic Bessemer works. The mechanical arrangements of the plant and general principles involved in the two processes are exactly alike, with the exception that the lining used in the basic process is a mixture of lime and magnesia, obtained by calcining dolomite. This is mixed with dry tar in suitable proportions, so as to make it bind, and is then either rammed into shape with hot tools, or pressed into bricks and baked as may be most convenient. The cast iron used should be as low in silicon as possible, on account of the injurious action of a silicious slag on the basic material of which the lining is composed. The phosphorus, on the other hand, may be as high as 3 p.c. without exerting any injurious effect on the finished product. To ensure low sulphur while the silicon is also low, about 1·5 p.c. of manganese is usually introduced into the iron. In modern works the proportion, both of silicon and of sulphur are reduced and rendered more uniform by the use of a metal mixer. The 'blow' is conducted in the early stages just as in the acid Bessemer process, silicon being removed first while carbon afterwards passes out, and the flame 'drops' as before. Lime is then added, and an after-blow is given, which lasts some 5 minutes, depending on the amount of phosphorus present; during this stage the phosphorus is almost completely removed and passes into the slag. The progress of the operation is judged by means of small samples which are withdrawn and examined at intervals during the after-blow. When ready, the metal is tapped as usual, and the product is a specially mild and soft metal. The slag is used, when ground to fine powder, as a phosphatic manure; it has also been used as a material for the construction of the bottoms of reheating furnaces (Harbord and Tucker's patent). The basic Bessemer process is applied on a large scale in this country, but is used still more extensively on the Continent, especially in the large steel works in the district around Düsseldorf on the Rhine.

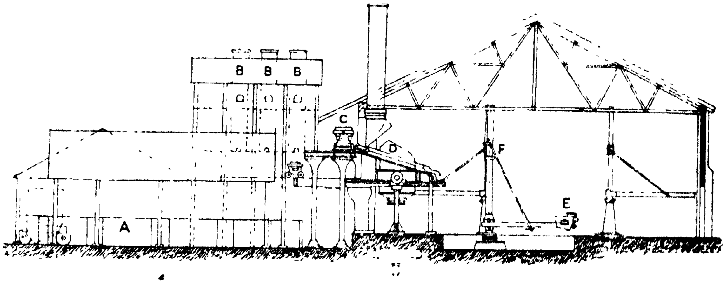


Fig. 5.

A, Shop or preparing Basic Lining; B, Cupolas for calcining Dolomite and remelting Iron; C, Ladle for Cast Iron; D, Bessemer Converter, E, Steel Ladle, F, Ladle Crane.

Where metal of special purity is required, the fluid steel, instead of being cast into ingots, may be transferred to an electric furnace, where with high temperatures and very basic slags the phosphorus may be reduced to a mere trace. After the phosphorus has thus been transferred to the basic oxidising slag, this slag is removed, and a slag is made of lime and fluor spar; carbon is also added and this reducing slag removes the sulphur. Hence by working with two slags in succession, one oxidising, and the other reducing, both phosphorus and sulphur can be removed, and a steel of special purity obtained. This method of working is employed at a number of American steel works.

In Bessemer's earlier experiments small converters were employed; some of which were moveable, whilst others were fixed. Both of these forms have been recently reintroduced, and small converters have met with considerable favour for special purposes, particularly for the production of steel castings.

Siemens steel. Numerous attempts have been made to prepare steel by decarburising cast iron by some method other than that previously described; but the only successful rival to the Bessemer process was originated by the late Sir William Siemens. The invention of the Siemens furnace, with the accompanying gas producers and regenerators, placed in the hands of the practical man the successful application of a beautiful scientific principle which has been largely used in many branches of manufacture, such as the production of glass, porcelain, and pottery; for the reheating of iron and steel, and for numerous other purposes. Space will not here allow of the description of the apparatus, and it will only be necessary to mention that by this means a temperature can be easily and economically obtained, which is amply sufficient to melt wrought iron, and to enable it to be readily poured when melted. Apart from the method used in heating the furnace, the Siemens-Martin process (which was invented by Siemens, and rendered commercially successful by Martin) closely resembles in principle the original puddling process. The furnace is of the same general shape as the puddling furnace, but is capable of working a charge of from 5 to upwards of 50 tons. The external portions are of cast iron lined with very refractory silicious firebrick, while the working bottom is of refractory sand. The pig iron to be used is charged first, and the malleable iron and iron ores which are added to decarburise the pig iron are introduced at suitable intervals during the operation, which generally lasts about 8-10 hours. Several modifications of the process have been introduced, it being convenient sometimes to omit either the malleable iron or the ore, whilst in some cases malleable iron or steel scrap only has been used (Martin's process). In any case, so long as a silicious lining is employed, the materials used must be as free as possible from phosphorus. The *basic process* is also conducted in the Siemens furnace, phosphoric pig iron, or similar metal from a mixer, being used, together with the necessary steel scrap and ore or other ferruginous oxidising materials. In larger establishments hand charging has now generally been replaced by mechanical appliances. For basic working the chief modification introduced is the substitution, for the ordinary silicious bed, of a working bottom of basic material, similar to that used in the basic Bessemer process. Quicklime is also added to the charge during the working of the heat so as to ensure a basic slag and the removal of the phosphorus. The open hearth process differs from the Bessemer basic process in that while in the latter the phosphorus remains in the fluid metal until practically all the carbon has been eliminated, in the open hearth process, on the other hand, much of the phosphorus is removed during the earlier stages of the operation. If the acid Siemens furnace may be regarded as a large puddling furnace with gaseous fuel, working on Cort's original lines, except that the temperature used is sufficiently high to melt the resulting malleable iron and so produce mild steel, then we may consider the basic Siemens process as closely resembling the 'pig boiling' of more recent times, except that, as in the previous case, the operation is on a much larger scale and the product is in a molten condition.

As compared with the Bessemer process the Siemens, or as it is frequently called, the 'open hearth' process, possesses the advantage that it is more under control, and for this reason is frequently preferred when work of a specially uniform character is required; it is also more in favour for steel castings. Further, it permits of the use of considerable quantities of scrap, which is relatively cheap, and would otherwise be a drug on the market. It also gives a greater yield per ton of metal used. This extra yield often more than pays for the cost of fuel used. The Bessemer plant, on the other hand, gives more rapid working, and hence is preferred for large outputs. There is little doubt that equally good steel may be produced by either of the processes, though the pneumatic method requires very careful attention when special uniformity is desired. In the United Kingdom the acid Siemens process is most important; in Germany the basic Bessemer is chiefly used; in America the two processes employed are the acid Bessemer for rails, &c., and the basic open hearth for structural materials. From the metal which is slightly too phosphoric to be used in the acid process an excellent steel is made in the basic open hearth furnace.

The tendency in recent years has been to replace the Bessemer process by the open hearth, and to develop the basic method of working.

The Talbot process. In this important modification of the open hearth basic process a large tilting furnace of cylindrical form is heated at either end by gaseous fuel and regenerators. The vessel, which holds 150 tons or more of fluid metal, is basic lined and a slag rich in molten oxides of iron is maintained. The charge of fluid cast iron is first worked till steel of the required composition is obtained; about 20 tons of this fluid steel is then tapped out of the furnace. Some 20 tons of metal is added to the contents of the furnace and a reaction is set up as a result of which silicon, carbon, and phosphorus are removed, and fluid steel remains. Metal is run off into the ladle as required for the rolling mills, and fresh iron poured in from time to time. The process is thus continuous, and the furnace works from week to week without stopping. The fuel consumption is low, the yield good, repairs are diminished, whilst steel of excellent quality can be produced from phosphoric ores.

Malleable cast iron. For many purposes where a complex form is necessary, and only moderate strength is required, the articles are cast in green sand in the ordinary way, but a special variety of pig iron is used, low in phosphorus, and manganese, and containing about 0·65 p.c. of silicon. The castings so prepared are white, hard, and brittle; but when heated, in contact with oxide of iron, in covered cast-iron boxes, to about 900° for several days, they become grey and soft. The softness so developed is accompanied with considerable malleability, so that the articles can be readily worked under the tool and punched, planed, &c., as required. Malleable cast iron, however, will not weld like ordinary malleable iron. This process is chiefly conducted in this country in the Midlands, particularly at Walsall and Birmingham, and the heating in contact with oxide of iron is known technically as 'annealing.' A portion of the graphite is removed by oxidation, and the rest, having been thrown out of solution at about 900°, exists as secondary graphite, or 'temper' carbon. In recent years the malleable cast iron industry has reached very large proportions in the United States, the output being now about ten times as great as that of the United Kingdom. The castings are generally produced from metal low in sulphur, but slightly higher in silicon than is usual with the European or 'Reaumur' process; it is melted in a coal-fired reverberatory, or in an acid Siemens furnace. The annealing is conducted at a temperature of about 750° and occupies a shorter time. Hence less graphite is removed by oxidation, and the product is known as 'black heart' castings.

Tin plates. In order to protect iron from oxidation it is frequently covered with a thin layer of metallic tin. This is chiefly applied to the protection of thin plates of steel, which are first rolled in the ordinary way, and, after a preparation (including 'pickling' in dilute sulphuric acid, annealing, and cold rolling) in order to obtain a suitable surface, the plates are immersed in a bath of molten tin which is kept covered with grease. In this way a thin coating of tin adheres to the surface of the iron and protects it from oxidation so long as the iron is completely covered. In case the tin is removed from any part of the surface, however, oxidation takes place more readily than in the original metal. For this reason galvanised iron is to be preferred for purposes where iron has to be exposed to atmospheric action, and where there is no chance of articles of food coming in contact with the zinc. Tin plates are largely manufactured in South Wales, and were formerly made from an iron possessing special malleability, and which was prepared in the old-fashioned open hearth. At present tin plates are prepared from mild steel, chiefly that produced by the Siemens process. (For details of preparation v. TIN PLATES.)

Galvanised iron. Iron which has to be exposed to the weather or other oxidising agencies is frequently galvanised, i.e. covered with a thin coating of metallic zinc. In this case the metal is previously cleaned from scale, &c., by being 'pickled' in hydrochloric acid, and after cleansing the article is immersed for a few moments in a bath of molten zinc, which is kept covered with a little ammonium chloride. By this means a uniform covering of zinc is obtained, which protects the iron underneath, not merely so long as the coating is perfect, but also when the zinc has been partly removed. Galvanised iron, however, cannot be used in contact with either mineral or vegetable acids, and hence is not employed for cooking utensils, nor for the cans in which food is preserved. Iron can also be coated with zinc by electro-deposition; or by heating at a moderate

ANALYSES OF PIG IRON.

Ore	Red hæmatite		Red mountain Alabama		Northants. Brown hæmatite		South Staffordshire All Mine (clay iron stone, cold blast)							Clay, iron stone (Dowlais)
Analyst . .	Greenwood		Leutscher		Henry	Turner	Tucker							Riley
Variety . .	No. 1	No. 2	No. 1	Grey forge	Grey	Grey	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	White	No. 3 Cold blast
Graphitic carbon	3·045	2·579	3·49	3·00	1·150	2·65	3·30	2·68	2·55	2·14	1·90	0·55	0·20	3·10
Combined carbon	0·704	1·175	0·07	0·57	0·554	0·08	0·40	0·45	0·40	0·50	0·56	1·70	2·00	0·04
Silicon . .	2·003	1·758	3·15	1·50	1·900	2·95	1·88	1·72	1·92	1·33	0·97	0·89	0·71	2·16
Manganese .	0·309	0·130	0·25	0·19	0·414	0·40	0·40	0·54	0·40	0·25	0·52	0·46	0·50	0·50
Phosphorus .	0·037	0·038	0·68	0·64	1·807	1·84	0·71	0·68	0·52	0·56	0·51	0·48	0·47	0·63
Sulphur . .	0·008	0·014	0·005	0·06	0·395	0·06	0·02	0·04	0·07	0·09	0·12	0·16	0·19	0·11
Metallic iron .	93·800	94·304	—	—	93·780	92·02	93·29	93·89	94·13	95·13	95·42	95·76	95·93	93·46

Ore	Carron Black band	Cleveland iron stone			Cinder	Dannemora magnetite	—	Mixed	Spanish	Cleveland	Carbonaceous
Analyst . .	M'Alley	Stead			Tucker	Henry	Tookey	Turner	Turner	Stead	Fleming
Variety . .	No. 1	No. 3	Forge	Mottled	Soft grey	White	Spiegeleisen	Silicon spiegel	Silicon pig	Silicon pig	Ohio softener
Graphitic carbon	3·00	3·70	3·40	2·90	2·90	—	} 5·04	1·71 }	1·12	3·15	2·85
Combined carbon	0·50	0·30	0·25	0·75	0·25	4·20			0·69	0·01	0·30
Silicon . .	1·96	2·50	2·10	1·00	2·84	0·08	0·41	8·72	9·80	4·48	5·90
Manganese .	1·71	0·72	0·50	0·47	0·44	0·10	7·57	16·92	1·95	0·72	1·00
Phosphorus .	0·69	1·50	1·60	1·60	2·80	0·05	0·16	—	0·21	1·97	1·10
Sulphur . .	0·04	0·04	0·06	0·15	0·05	trace	0·08	—	0·04	0·01	0·02
Metallic iron .	92·10	92·00	92·28	92·75	90·72	95·57	86·74	71·87	86·19	89·66	88·83

ANALYSES OF WROUGHT IRON, STEEL, &C.

Description	Special strong foundry iron	Refined iron	Puddled bar	Wrought iron	Basic Bessemer metal, end of blow	Bessemer soft steel	Mushet steel, self hardening
Locality . .	-	Bromford	S. Stafford	S. Stafford	S. Stafford	Neuberg	Sheffield
Authority . .	Turner	Dick	Turner	Turner	Walton	Greenwood	Hadfield
Carbon (combined)	0·47	3·07	0·10	0·06	0·02	0·126	2·00
Silicon . .	1·43	0·63	0·13	0·04	0·01	0·135	1·60
Manganese .	1·04	trace	0·08	0·08	0·06	0·158	1·72
Phosphorus .	0·58	0·73	0·35	0·20	0·04	0·060	-
Tungsten . .	—			—		—	8·22
Sulphur . .	0·07	0·16	0·05	0·05	0·04	0·014	0·02
Iron . .	—	95·14	99·29	99·57	99·83	—	—

Description	Siemens soft steel	Bessemer steel rails	Siemens steel tyres	Silicon cast steel	Crucible steel for forgings	Hard tool steel
Locality . . .			Sheffield	Terre Noire	—	—
Authority . .	Greenwood	Greenwood	Turner	Pourcel	Greenwood	Greenwood
Carbon . . .	0·167	0·21	0·58	0·61	0·36	1·144
Silicon . . .	0·023	0·047	0·23	0·23	0·02	0·166
Manganese . .	0·044	0·36	0·64	0·70	0·30	0·104
Phosphorus . .	0·062	0·035	0·03	0·12	0·03	—
Sulphur . .	0·013	0·052	0·03	0·05	0·02	—
Iron . . .	—	—	98·49	-		-

ANALYSES OF VARIOUS SLAGS

Material	Blast furnace cinders			Refinery slag	Tap cinder	Mill cinder	Bessemer slag end of blow
	With white iron	Grey iron	Cold blast grey iron				
Locality	Dowlais	Cleveland	South Stafford	Dowlais	Dowlais	Dowlais	—
Authority . . .	Riley	Bell	Percy	Riley	Riley	Riley	Snelus
Silica	43·07	29·92	39·52	25·77	7·71	28·71	46·75
Alumina . . .	14·85	21·70	15·11	3·60	1·63	2·47	2·80
Ferrous oxide .	2·53	0·32	2·02	65·52	66·32	66·01	16·86
Ferric oxide . .	-	—	-		8·27	—	—
Manganous oxide .	1·37	0·80	2·89	1·57	1·29	0·19	32·23
Lime	28·92	38·72	32·52	0·45	3·91	0·81	1·19
Magnesia . . .	5·87	6·10	3·49	1·28	0·34	0·27	0·52
Potash . . .	1·84	—	1·06		—	—	—
Calcium sulphide . .	1·90	-	2·15	-	-	-	-
Phosphorus pentoxide .	—	0·07	—	1·37	8·07	1·22	0·01
Sulphur . . .	—	1·61	—	0·23	1·78	0·11	trace

temperature with zinc-dust; this process is known as 'sherardising.' (For further details v. ZINC.)

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T. T.

Iron as produced by the reduction of its oxides by carbon always contains more or less of the latter element. Wrought iron is the purest form of commercial iron, but in addition to carbon it usually contains small quantities of sulphur, phosphorus, silicon, &c. Chemically pure iron may be obtained as a black powder devoid of metallic lustre by reducing the oxide or oxalate in a current of hydrogen which is pyrophoric if the reduction is effected at a low temperature.

Pure iron finds a limited use in transformer cores and for experimental work. It is usually prepared by electrolysis, the electrolyte consisting of a solution of ferrous chloride and calcium chloride, or a mixture of ferrous ammonium sulphate, magnesium, and sodium hydrogen carbonate, the working temperature being 90° and current density 10 amps. per dm.^{2}.

Pure iron has a silver-white lustre and is capable of a high polish. It is highly ductile and malleable, becomes soft at a red heat, and may be welded at a white heat; m.p 1530° (Dana and Foote). It may be distilled in the electric furnace. It is attracted by the magnet but is not permanently magnetic. It seems to exist in three allotropic forms, distinguished as α-, β-, and γ-ferrite, depending on temperature (Osmond and Cartaud). Sp gr. 7·86; mean sp.h. 0·1098 (15°-100°) increasing rapidly up to 850°, when it decreases.

COMPOUNDS OF IRON

Oxides. Three oxides of iron are known :—

Ferrous oxide or iron monoxide FeO ;

Ferric oxide or iron sesquioxide Fe_2O_3 ;

Ferroso-ferric oxide or magnetic oxide of iron Fe_3O_4.

The trioxide FeO_3, which may be considered to exist in the ferrates, has not been isolated.

Iron monoxide or **ferrous oxide** FeO is a strong base. It may be prepared by the reduction of the sesquioxide in a current of hydrogen at 300°. On exposure to air it oxidises with incandescence, but loses this property when allowed to remain for 12 hours in an atmosphere of hydrogen. It is also obtained as a black, velvety powder by adding ferrous oxalate to boiling caustic potash solution; when washed with water in air it takes up oxygen. Ferrous oxide is also formed by the action of nitrous oxide on metallic iron at 200° (Sabatier and Senderens, Compt. rend. 1892, 114, 1429).

The hydrated oxide $Fe(OH)_2$ is precipitated on addition of caustic soda to a ferrous salt in absence of air. When absolutely pure the precipitate is white, but it rapidly absorbs oxygen, acquiring a greenish hue and becoming ultimately converted into the red sesquioxide. It crystallises from a strong caustic soda solution in flat, pale green prisms (de Schulten, Compt. rend. 1889, 109, 266).

Ferrous oxide absorbs carbon dioxide with avidity. It dissolves in about 150,000 parts of water. It is used to impart a green colour to glass, which at the same time becomes athermanous, transmitting but little heat (Zsigmondy, Dingl. poly. J. 287, 17 *et seq*).

Ferroso-ferric oxide, *Magnetic oxide*, *Black oxide* ($FeO{\cdot}Fe_2O_3$ or Fe_3O_4, occurs in nature as *magnetite* (*magnetic iron ore* or *lodestone* (*q.v.*)) in most parts of the world, and constitutes one of the most important ores of iron. It is always attracted by the magnet, but does not always possess the property of attracting iron. It may be prepared by passing steam or carbon dioxide over red-hot iron, but the primary product in the case of water vapour is FeO. It is probably a coating of Fe_3O_4 which renders iron 'passive,' or unacted upon by concentrated nitric acid or water. This property is taken advantage of in the Bower-Barff process for preventing the rusting of iron, in which the metal is heated to redness and subjected to the action of steam.

When pure this oxide is an iron-black substance having a sub-metallic lustre. Its sp.gr. is 5·18, and its melting-point is 1527° (Kohlmeyer, Metallurgie, 1909, 6, 323).

The oxide is soluble in strong acids, the solutions containing a mixture of ferrous and ferric salts. By adding caustic alkali to such a solution or to a mixture of ferrous and ferric chlorides in proper proportions, a black precipitate of *ferroso-ferric hydroxide* is obtained, which, on drying in air, yields a brown-black, brittle mass, stable in air, which is magnetic, and may thus be separated from admixed ferrous and ferric oxides. It has the composition $Fe(OH)_2{\cdot}Fe_2O_3$.

Iron-scale is a compound of ferrous and ferric oxides in varying proportions. The inner layers are not magnetic, and approximate in composition to $6FeO,Fe_2O_3$; the outer layers of the scale are magnetic, and contain a larger proportion of ferrous oxide.

Iron sesquioxide or **ferric oxide** Fe_2O_3 occurs anhydrous as *hæmatite*, sp.gr. 5·19–5·25, *specular iron ore*, *kidney ore*, and *micaceous iron ore*, and, in the hydrated condition, as the yellow or brownish *limonite* $2Fe_2O_3,3H_2O$, of which *bog iron ore*, *pea iron ore*, and certain *clay iron stones* are earthy varieties. *Göthite* Fe_2O_3,H_2O and *turgite* $2Fe_2O_3,H_2O$ are other forms in which the hydrated oxide occurs. The earthy varieties of hæmatite are known as *reddle* or *ruddle*, and as *red ochre*, and are used as pigments; the earthy varieties of limonite being similarly used under the names *yellow* and *brown ochre*.

The anhydrous oxide may be obtained by heating the hydrated oxide or a ferrous or ferric salt containing a volatile acid. The latter method is the one principally used for the preparation of the commercial oxide, the salts most used being the sulphate or the chloride obtained from the 'pickling' of iron in the process of galvanising.

It may be prepared in small crystals by passing the vapour of ferric chloride over heated lime. The ignited or native oxide is slowly soluble in acids, the best solvent being a mixture of 8 parts sulphuric acid and 3 parts water.

Ferric oxide crystallises in tabular rhombohedral scales of sp.gr. 5·17, having a steely lustre. At the edges the crystals transmit light of a ruby-red colour. The solidifying-point of the molten oxide is 1562°-1565° (Kohlmeyer, Metallurgie, 1909, 6, 323).

Heated in the electric furnace or in the oxyhydrogen flame it yields the magnetic oxide (Moissan, Compt. rend. 1892, 115, 1034; Read, Chem. Soc. Trans. 1894, 314). Usually it is very slightly paramagnetic, but it is more strongly magnetic if prepared by the oxidation of ferrous hydroxide (Malaguti, Compt. rend. 1862, 55, 350). Walden states that at 1350° the dissociation pressure of the oxide is about equal to that of the oxygen in the air (J. Amer. Chem. Soc. 1908, 39, 1350).

The residue obtained in the manufacture of Nordhausen sulphuric acid by distillation of ferrous sulphate consists of this oxide, and is known as *colcothar*, and is largely used as a pigment. On account of the absence of grit it is used as polishing *rouge*; the parts which are of a scarlet colour—*i.e.* which have not been strongly heated—being preferred for glass polishing and for jewellery, &c., whilst the more strongly heated parts, which possess a bluish tint, are employed under the term *crocus* for polishing metals. It has been shown that these variations in colour are due to the varying size of the grains (Wöhler and Condrea, Zeitsch. angew. Chem. 1908, 21, 481).

Ferric oxide acts as a catalyst in promoting the combination of sulphur dioxide and oxygen, and a process for the preparation of sulphuric acid has been based upon this reaction (Lunge and Reinhardt, Zeitsch. angew. Chem. 1904, 17, 1041; *see* also Keppeler, d'Ans, Sundell, and Kaiser, *ibid.* 1908, 21, 532, 577; Keppeler and d'Ans, Zeitsch. physikal. Chem. 1908, 62, 89). This oxide is also used in some forms of accumulator (*see e.g.* D. R. PP. 180672 and 190236; also Peters, Chem. Zentr. 1908, i. 213).

The use of ferric oxide for standardising solutions of permanganate has been proposed by Brandt, who describes a method for the preparation of the pure substance (Chem. Zeit. 1908, 32, 812 *et seq.*).

Ferric oxide is invariably present in considerable quantities in *copper paint* (*v.* COPPER OXIDES).

This oxide may be combined with the monoxides of calcium, magnesium, zinc, copper, and other metals. The resultant oxides, which are prepared usually by fusing the mixed oxides, are always magnetic, and correspond in composition with the magnetic iron oxide. The oxide containing magnesium $Fe_2O_3 \cdot MgO$ occurs naturally as *magnoferrite*, and that containing zinc and manganese is found as *Franklinite* (*see* Percy, Phil. Mag. 1873, [iv.] 45, 455; and List, Ber. 1878, 11, 1512).

Solutions of alkali ferrites are obtained by boiling solutions of the ferrates or by boiling ferric hydroxide in strong caustic alkali solution (Haber and Pick, Zeitsch. Elektrochem 1900, 7, 215; 1901, 7, 724).

The hydrated oxide is best prepared by precipitating a solution of ferric chloride with excess of ammonia. It forms a bulky, brown, slimy precipitate, which shrinks considerably in drying. It slowly gives up its water at 320°, and if heated to dull redness when anhydrous, suddenly contracts and glows brightly, becoming much less soluble in acids; this is probably due to an allotropic change which is known to take place at 640° (Keppeler and d'Ans, Zeitsch. physikal. Chem. 1908, 62, 89; *see* also *ibid.* 641).

Freshly precipitated ferric hydroxide, when heated with water under a pressure of 5000 atmospheres gives the following products:—

At 30°–42·5° limonite,

At 42·5°–62·5° göthite,

And above 62·5° targite or hydrohæmatite (Ruff. Ber. 1901, 34, 3417).

A 'yellow hydrate,' which, under these conditions is unchanged between 40° and 70°, can be obtained by the oxidation of moist ferrous hydroxide or carbonate (Muck, Zeitsch. Chem. 1868, [ii.] 4, 41; Tommasi, Ber. 1879, 12, 1299, 2334).

When the hydrated oxide is merely allowed to remain for some months under water, a crystalline powder containing $Fe_2O_3(OH)_6$ is obtained which corresponds to the native limonite. This hydrate is the colouring ingredient of yellow clays, &c., and constitutes the precipitate from chalybeate streams. It may also be obtained by precipitation from a cold solution of a ferric salt and drying, without the aid of heat, over sulphuric acid.

The freshly precipitated oxide is readily soluble in acids and in concentrated solutions of ferric salts. The solution in ferric chloride, when containing excess of oxide, may be slowly dialysed with separation of a dark red liquid in which the ratio of chlorine to iron corresponds to the composition $82Fe(OH)_3 : FeCl_3$ (Linder and Picton, Chem. Soc. Trans. 1905, 1920). A similar solution containing a small amount of acetate is prepared by dialysing ferric acetate, and is used medicinally as *dialysed iron* or *liquor ferri dialysati*.

A colloidal solution of pure ferric hydroxide may be obtained from the dialysed solution containing chlorine by electrolysis under special conditions (Tribot and Chrétien, Compt. rend. 1905, 140, 144). The solution is gelatinised by alkalis and by many acids and salts, even in very small amounts (*see* also Gilotti, Gazz. chim. ital. 1908, 38, ii. 252).

Soluble metaferric hydroxide $Fe_2O_4H_2$ is obtained by heating a solution of ferric nitrate to 100° for 3 days, and then adding a few drops of hydrochloric acid. The hydroxide is thus precipitated, and when dried on a porous tile forms black scales, which dissolve in water to a tasteless red liquid (Pean de St. Gilles, Ann. Chim. Phys. 1856, [iii.] 46, 47; Scheurer-Kestner, *ibid.* 1859, [iii.] 57, 23; Debray, Compt. rend. 1869, 68, 913).

A similar solution can be prepared by boiling a solution of ferric nitrate with copper filings or zinc-dust (Cohen, J. Amer. Chem. Soc. 1914, 36, 19).

The hydrated oxide combines with sugar, forming a soluble compound, thus lowering the percentage of crystalline sugar obtained from the pans and raising the proportion of molasses. On this account raw sugar is soon injured by contact with iron vessels, and even the clearing 'char' should be as free as possible from iron. According to Schachtrupp and Spunt (Pharm. Centralhalle, 1893, 11, 148) the hydroxide is soluble only in solutions of invert sugar, and cannot itself cause inversion, though this may be brought about by anhydrous ferric oxide.

The hydrated oxide is largely used for removing sulphuretted hydrogen from coal gas. A hydrated sulphide is thus produced with evolution of water. When the oxide ceases to absorb the gas, it is exposed to a current of air, care being taken to prevent great rise of temperature, and the oxide is reproduced with separation of free sulphur. The large quantity of Prussian blue contained in the spent 'oxide' is now used for the production of cyanides (*q.v.*).

A yellowish-brown hydrated sesquioxide, precipitated on calico by the action of caustic soda on ferrous sulphate, is known as *chamois* or *rouille*.

Iron rust when completely oxidised has a composition approximating to that of limonite, but when freshly formed contains much hydrated ferrous oxide and carbonate.

In pure water, free from air, the rusting of iron is purely electrolytic and does not proceed beyond a concentration of Fe equal to $1{\cdot}2+10^{-6}$ gram-mol. per litre. The presence of oxygen gives rise to a new e.m.f.; carbon dioxide plays a secondary part, affecting the very variable composition of the rust and its presence is not essential; hydrogen peroxide need not be formed. The corrosion is most rapid when both air and water are in direct contact with the metal Caustic soda and sodium carbonate stop corrosion; ammonium salts accelerate it. *Cf.* art. CORROSION OF METALS.

Ferric acid H_2FeO_4 is only known in combination. The potassium salt is produced with evolution of considerable heat by heating the sesquioxide with potassium nitrate or hydroxide, or with a mixture of the two substances (Fremy, J. Pharm Chim. 1841, 27, 97; Hofmann, Ber. 1869, 2, 239).

It may be prepared by the electrolytic oxidation of iron in caustic potash solution (Haber and Pick, Zeitsch. Elektrochem. 1900, 7, 215), or by passing chlorine through a suspension of ferric hydroxide in caustic potash.

Barium ferrate is the most stable salt of ferric acid, and is obtained as a dark red powder by precipitating a solution of sodium ferrate with barium chloride (Baschieri, Gazz. chim. ital. 1906, 36, ii. 282).

Ferrous sulphide FeS is found in certain meteorites. It may be considered to exist in combination with the sesquisulphide in *pyrrhotine* or *magnetic pyrites*, and in combination with other sulphides in other minerals. It is found in considerable quantities in the black deposit in cesspools, &c., being produced by the action of organic matter on ferruginous bodies or iron oxide in presence of sulphates In meteorites it occurs as the mineral *troilite*.

It may be prepared by heating a mixture of iron filings and sulphur or of ferrous sulphate and charcoal; by stirring a white-hot rod of wrought iron in melted sulphur; by heating other iron sulphides to bright redness in hydrogen, or by precipitating ferrous salts with alkaline sulphides or sulphuretted hydrogen. In the compact state, ferrous sulphide is a very hard, metallic-looking black, or nearly black crystalline solid of sp.gr. 4·69. It has a metallic lustre with a yellowish reflex, and sometimes occurs in hexagonal prisms. It is not magnetic, is permanent in air, and fusible at a full red heat. The precipitated sulphide, however, is readily oxidised to sulphate in air, especially when moist.

It is decomposed by acids with evolution of sulphuretted hydrogen, and is usually employed for the preparation of that gas.

Ferrous sulphide forms the main constituent of *iron lute* (*v.* LUTES).

Ferroso-ferric sulphide $FeS{\cdot}Fe_2S_3$ forms one of the varieties of *pyrrhotine*: it is obtained when iron pyrites is heated out of contact with air for the production of sulphur. *Magnetic pyrites* $5FeS{\cdot}Fe_2S_3$ or $6FeS{\cdot}Fe_2S_3$ occurs in hexagonal plates of a brassy colour. It is attracted by the magnet and has sp.gr. 4·4–4·7.

Ferric sulphide Fe_2S_3 is obtained by gently heating a mixture of iron and sulphur or by the action of sulphuretted hydrogen on the sesquioxide below 100°, and may be prepared by pouring a solution of ferric salt into excess of ammonium sulphide. By the latter reaction it is formed in the purification of coal gas (Gedel, J. Gasbel. 1905, 48, 400; Stokes, J Amer. Chem. Soc. 1907, 29, 304). It combines with other sulphides of iron, and with the sulphides of silver, potassium, and sodium. The hydrated sulphide is rapidly decomposed by air, and in absence of air undergoes spontaneous decomposition into ferrous sulphide and iron disulphide. The anhydrous sulphide is pyrophoric if suddenly brought into contact with air

Potassium ferric sulphide $K_2Fe_2S_4$ is obtained when iron filings, potassium carbonate, and sulphur are heated together and the mass extracted with water It is thus obtained in purple-coloured, needle-shaped crystals of sp.gr 2·863, which burn when heated in air

Sodium ferric sulphide $Na_2Fe_2S_4,4H_2O$ is obtained in a similar way and forms brown microscopic needles. It occurs in the 'black-ash liquors' of the Leblanc process.

Cuprous ferric sulphide $Cu_2S{\cdot}Fe_2S_3$ occurs native as '*copper pyrites*.'

Iron disulphide FeS_2 occurs in immense quantities as *iron pyrites* or *mundic* in hard, yellow, brassy cubes, sp.gr. 5·185; or in other forms of the regular system, and in masses of various shapes, frequently known as 'thunderbolts.' This mineral, as well as *marcasite* or *white iron pyrites* (sp gr. 4 68–4·85), and other minerals of the same composition, but crystallising in the rhombic system, is produced in nature by the reduction of ferrous sulphate by organic matter, and is therefore often found forming fossils in peat, chalk, &c., and in clay, containing much organic matter. Marcasite may be prepared artificially by heating ferrous sulphide with sulphur; by passing hydrogen sulphide over the oxides or chlorides of iron at a red heat; by the action of carbon disulphide vapour on heated ferric oxide or by heating ferric chloride with phosphorus pentasulphide (Glatzel, Ber. 1890, 23, 37).

Pyrites is quite permanent in air, but marcasite slowly becomes oxidised and disintegrated on exposure. Iron pyrites is largely employed as a source of sulphur in the manufacture of sulphuric acid, ferrous sulphate, &c. (*v.* SULPHURIC ACID; SULPHUR).

By heating iron disulphide with aluminium powder in a stream of hydrogen sulphide the compound Al_2FeS_4 is obtained (Houdard, Compt. rend. 1907, 144, 801; *see* also Ditz, Metallurgie, 1907, 4, 786).

Iron sub-sulphide Fe_4S_3 is obtained when iron is heated in the vapour of carbon disulphide. It forms a crystalline mass of sp.gr. 6·957, and dissolves in dilute acids with evolution of hydrogen and hydrogen sulphide (Gautier and Hallopeau, Compt. rend. 1889, 108, 806).

Ferric arsenide occurs in nature as *lölingite*

$FeAs_2$, and with sulphur as *mispickel* or *arsenical pyrites* Fe_2AsS, from which the greater part of the arsenic of commerce is obtained (*v.* ARSENIC). Arsenic combines directly with iron.

Compounds of carbon, phosphorus, silicon, and nitrogen with iron are also known. The effects produced on the properties of iron and steel by the three first-named elements are described under the manufacture of iron.

Iron nitride Fe_2N (Stahlschmidt, Pogg. Annalen, 1864, 125, 37) is obtained by the action of excess of ammonia at 420° on ferrous chloride or bromide, reduced iron, or iron amalgam, as a dull grey powder (Fowler, Chem. Soc. Trans. 1901, 285).

It may be prepared in the compact state by heating iron wire or rod to a bright red heat in a large excess of ammonia. The product is so brittle that it can be powdered, and has sp.gr. 6·0–6·5. When heated in air it is oxidised, and it ignites when warmed in chlorine. Dilute acids dissolve it with the formation of ferrous and ammonium salts (Beilby and Henderson, Chem. Soc. Trans. 1901, 1249; Guntz, Compt. rend. 1902, 135, 738).

Phosphides of iron. A phosphide Fe_2P is produced by heating a mixture of ferrous or ferric phosphate under common salt or by heating iron filings with cuprous phosphide in the electric furnace. It forms lustrous grey crystals, probably hexagonal in form; sp.gr 6·56; m.p. 1290° (Maronneau, Compt. rend. 1900, 130, 656; Le Chatelier and Wologdine, *ibid.* 1909, 149, 709). Heated in air it forms the basic phosphate $2Fe_2O_3,P_2O_5$.

When iron is heated in phosphorus vapour, or the monosulphide is heated in hydrogen phosphide gas, the phosphide FeP is formed. It is a dark grey powder of sp.gr. 5·76.

Another phosphide Fe_2P_3 is formed by strongly heating phosphorus and ferric chloride vapours in a current of carbon dioxide (Granger, Compt. rend. 1896, 122, 936); or by the action of the vapour of phosphorus iodide on finely divided iron. It forms hard, non-magnetic, steel-grey crystals; sp.gr. 4·5.

A phosphide Fe_3P of sp.gr. 7·74 and m.p. 1110° has also been described (Le Chatelier and Wologdine, *l.c.*).

Iron borides. Two borides of iron have been described:

Fe_2B forms steel-grey prisms; sp.gr. 7·37 at 18°. It is oxidised by dry air at a red heat and by moist air at the ordinary temperature.

FeB_2 has not been obtained pure, but has sp.gr. *circa* 5, and is extremely hard (Binet du Jassonneix, Compt. rend. 1907, 145, 121).

Iron silicide $SiFe_2$ (ferro-silicon) is produced by heating iron with silicon, or with silica and carbon, in the electric furnace (Moissan, Compt. rend. 1895, 121, 621; Bertolus, Fr. Pat. 393, 818, 1908). It forms grey magnetic prisms of sp.gr. 7, and is readily attacked by acids.

Several iron-silicon compounds are known, viz. Fe_2Si, FeSi, and $FeSi_2$. Two eutectics are known, the first containing 21·6 p.c. Si and composed of Fe_2Si and FeSi, the second containing 60 p.c. Si and composed of FeSi and Si.

Under certain circumstances commercial ferro-silicon may evolve the gaseous hydrides of arsenic and phosphorus (present as impurities) with very bad effect on human beings (*e.g. see* J. Soc. Chem. Ind. 1909, 25; Pellew, *ibid.* 1914, 774). The tendency to decomposition is not so marked in alloys containing less than 30 p.c. Si; the richer alloys over 65 p.c. Si are also less liable to spontaneous disintegration (Anderson, Eng. and Min. J. 1917, 103, 1095).

Iron carbide (*see* CEMENTITE and STEEL).

FERROUS SALTS.

Anhydrous ferrous salts are usually colourless; the hydrated salts are greenish or blue. The solutions are sweet and astringent and ink-like in taste, and form powerful reducing agents.

Ferrous chloride $FeCl_2$ may be prepared by passing dry hydrogen chloride over red-hot iron or by reducing ferric chloride in a current of hydrogen, when the anhydrous salt is deposited in colourless shining scales, sp.gr. 2·528, which are very deliquescent and easily soluble in water and alcohol. It fuses at a red heat, and volatilises at a yellow heat, the V.D. being 6·4–6·6 (V. Meyer, Ber. 1884, 17, 1335). At 1300°–1500° the V.D. is normal = 4·3 (Nilson and Pettersson, Chem. Soc. Trans. 1888, 827).

In solution it is obtained by dissolving iron in hydrochloric acid. It crystallises in deliquescent, bluish-green, monoclinic crystals, sp.gr. 1·93, containing 4 molecules of water.

Solutions of ferrous chloride in strong hydrochloric acid are partially converted into ferric chloride by sulphur dioxide. The reaction is reversible:

$$4FeCl_2+SO_2+4HCl \rightleftarrows 4FeCl_3+S+2H_2O$$

(Wardlaw and Clews, Chem. Soc. Trans. 1920, 117, 1093).

The anhydrous salt absorbs ammonia to form the compound $FeCl_2{\cdot}6NH_3$, which gives off ammonia at 100°, and at higher temperatures yields ammonium chloride, nitrogen, and iron nitride (Fowler, Chem. Soc Trans. 1901, 288). It combines with bromine to form the unstable compound $FeCl_2Br$ (Lenormand, Compt. rend. 1893, 116, 820).

Ferrous bromide $FeBr_2$ is obtained as a yellowish crystalline solid by the union of its elements. The hydrated bromide crystallises in bluish-green rhombic tablets with 6 molecules of water.

Ferrous iodide FeI_2 is obtained by heating iron with iodine as a grey lamino-crystalline mass; m.p. 177° (Carius and Wanklyn, Annalen, 1861, 120, 69).

Ferrous sulphite $FeSO_3$. Iron dissolves in aqueous sulphurous acid in absence of air, with formation of ferrous sulphite and thiosulphate. The latter salt is very soluble, but the sulphite is deposited in greenish crystals.

Ferrous sulphate, green vitriol, or **copperas.** $FeSO_4,7H_2O$, occurs as *melanterite*, being derived from the decomposition of the native sulphide, especially of marcasite, and is manufactured by the oxidation of pyrites by air and rain.

The pure salt is prepared by heating an excess of iron wire or 1½ parts of precipitated ferrous sulphide in 1½ parts of sulphuric acid diluted with four times its weight of water. The solution is acidified if necessary, and is filtered quickly. Bluish-green monoclinic crystals containing $FeSO_4,7H_2O$, and having a sp.gr. of 1·889 at 4° (Joule and Playfair), are thus produced.

It is prepared on the large scale by dissolving scrap iron in warm sulphuric acid of 1·150 sp.gr., and concentrating the nearly neutral solution. The liquid is settled, quickly drawn off, allowed to clear for 24 hours, and run into crystallising tanks, in which strings, straws, or wooden laths are suspended to induce crystallisation. The crystals are washed with a minimum quantity of water and dried.

When sulphur is distilled from iron pyrites, the residue, known as *sulphur waste*, is laid upon inclined shelves in contact with air to oxidise. The weathered mass is levigated, and the ferrous sulphate is crystallised out.

Large quantities of this sulphate are obtained in the manufacture of copper sulphate (*v.* COPPER), and small quantities in the preparation of sulphuretted hydrogen for precipitating arsenic from sulphuric acid.

Ferrous sulphate is obtained at Fahlun during the extraction of copper sulphate from mine water, and also from the runnings of other mines.

The *Salzburg vitriol* prepared at Buxweiler contains ferrous and copper sulphates (*v.* COPPER). The copper may be separated as metal and any excess of acid converted into sulphate by the addition of scrap iron to the liquid.

Crude ferrous sulphate always contains ferric sulphate, which gives the crystals a more decided green colour; they are frequently coated with a yellow deposit due to oxidation. By washing with absolute alcohol, this deposit, being soluble, is removed, and the crystals are rendered more permanent.

The pure salt may be obtained in the most permanent condition by precipitating a concentrated aqueous solution by addition of excess of alcohol and washing the precipitated crystals with nearly absolute alcohol. It can be obtained perfectly pure and dry, by powdering an ordinary sample and repeatedly pressing it between filter paper. It is quite stable in air at 15°, and neither oxidises nor effloresces, or deliquesces (De Forcrand, Compt. rend. 1914, 158, 20). The presence of even a trace of ferric salt increases the liability of the crystals to oxidation. The crystals contain 7 molecules of water and are monoclinic, of sp.gr. 1·889 at 4°. Another hydrate contains $5H_2O$ and crystallises in the triclinic system, being isomorphous with $CuSO_4,5H_2O$. Ferrous sulphate may be obtained in rhombic prisms containing 4 molecules of water, isomorphous with zinc sulphate. Crystals may also be produced containing 3 and 2 molecules of water. The monohydrate is obtained when the heptahydrate is allowed to effloresce over conc. sulphuric acid, or when it is melted in its water of crystallisation and allowed to solidify (Etard, Compt. rend. 1878, 87, 502; Scott, Chem. Soc. Trans. 1897, 564).

When gradually heated to 140° *in vacuo* it loses 6 molecules of water and becomes colourless, but the remaining molecule is not removed at 260°, and, except when heated in small quantities, it is impossible to render the salt anhydrous without loss of acid. At a red heat a basic sulphate is produced, with evolution of sulphur trioxide, and, at higher temperatures, ferric oxide is left. A complete investigation of the dissociation of ferrous sulphate has been made by L. Wöhler, Plüddemann, and P. Wöhler (Ber. 1908, 41, 793).

Ferrous sulphate is insoluble in absolute alcohol. Its solubility in 100 parts of water is

10°	15°	25°	32·5°	46°	60°	90°	100°
61	70	115	151	227	263	370	333

The reduced solubility at 100° may be attributed to partial dehydration or dissociation.

The aqueous solution slowly oxidises on exposure to air, and deposits a yellowish, highly basic ferric sulphate, leaving the normal ferric sulphate in solution. The acid finally becomes divided between the precipitated salt and that in solution, rendering the former less basic but still insoluble, and converting the normal salt into a soluble basic sulphate. Ferrous sulphate, like the chloride, absorbs nitric oxide in solution. The gas is given off in a vacuum, or when the solution is heated, but it probably forms the compound $FeSO_4 \cdot NO$. When such a solution is mixed with sulphuric acid and cooled a purple-red colour is produced, which is used in the well-known ring test for nitrates (*see* also Machot and Zechentmacher, Annalen, 1906, 350, 368).

On account of its reducing power, ferrous sulphate precipitates gold and palladium from solution, and reduces indigo to the leuco compound.

Ferrous sulphate is largely used in dyeing and tanning, and in the manufacture of inks (*v.* INK), Prussian blue, red oxide of iron, and other pigments. In weak solution it is said to promote the growth of certain plants, especially of roots. When added to excremental matters it absorbs ammonia and other volatile substances, and renders the matter almost odourless. It is used for the treatment of sewage (*see e.g.* Pochin and Richardson, Eng. Pats. 15239 and 17970, 1908).

In dyeing textiles, leather, wood, &c., it is largely used for the production of various shades of black, grey, lilac, and brown. It is used as a mordant for the production of Prussian blue in calico-printing, and is the raw material from which acetates, nitrosulphates, and other iron mordants are prepared.

Ferrous disulphate FeS_2O_7 is separated as a white powder on addition of excess of concentrated sulphuric acid to a concentrated aqueous solution of the normal sulphate. On addition of water it is decomposed into the normal salt and free acid (Bolas, Chem. Soc. Trans. 1874, 812).

With ammonium and potassium sulphates, ferrous sulphate produces double salts containing 6 molecules of water and of great stability and fine crystalline form.

Ferrous ammonium sulphate

$$FeSO_4,(NH_4)_2SO_4,6H_2O$$

is prepared by dissolving molecular proportions of the two sulphates in the minimum quantity of hot water, filtering hot, and crystallising. It forms fine bluish-green monoclinic crystals of sp.gr. 1·813, of which 100 parts of water dissolves 21·6 parts at 20° and 56·7 parts at 75°.

The double salt is permanent in air, particularly when precipitated by addition of alcohol to the concentrated aqueous solution and washed with absolute alcohol, and is used by chemists in place of ferrous sulphate, especially for standardising solutions.

Ferrous phosphate $Fe_3(PO_4)_2,8H_2O$ occurs as *Vivianite* or *blue iron earth*, sometimes mixed with clay and peat or associated with bog iron ore. It may be produced by addition of sodium phosphate to ferrous sulphate. The fresh precipitate is used medicinally. When quite pure it is colourless, but it rapidly becomes bluish or green from oxidation. When iron is dissolved in phosphoric acid the solution deposits colourless needles of $Fe(H_2PO_4)_2,2H_2O$, which rapidly alter in air (Erlenmeyer, Annalen, 1878, 194, 182).

Ferrous arsenate prepared from ferrous sulphate and sodium arsenate has been proposed for use as an insecticide, for which purpose it has many advantages over Scheele's green (Vermorel and Dantony, Compt. rend. 1909, 148, 302).

Ferrous carbonate $FeCO_3$ occurs as *spathic iron ore*, together with the carbonates of lime, magnesia, and manganese. *Clay iron stone* is an argillaceous ferrous carbonate

Ferrous carbonate dissolves in water containing free carbonic acid, the acid salt so produced being the essential constituent of chalybeate waters. The solution is decomposed rapidly on boiling and slowly on exposure to air, with precipitation of an ochreous deposit of the hydrated oxide, which, in the case of mineral waters, frequently contains organic matter and ferric arsenate, and is occasionally found to contain antimony.

Spathic iron ore can be obtained artificially in microscopic rhombohedra by precipitating ferrous sulphate with sodium hydrogen carbonate and heating the solution for 12–36 hours at 150°. When sodium carbonate solution is added to ferrous sulphate solution a flocculent white precipitate is obtained which rapidly becomes green, and is ultimately completely converted into ferric hydroxide.

Ferrous nitrate $Fe(NO_3)_2,6H_2O$ is prepared by dissolving ferrous sulphide in dilute nitric acid, or, preferably, by addition of barium nitrate to ferrous sulphate solution.

The solid salt is very soluble in water and very unstable, changing to ferric nitrate. The action between iron and dilute nitric acid does not result in the formation of ferrous nitrate, and is extremely complicated (Montemartini, Chem. Soc. Abstr. 1892, 1278).

Cyanogen compounds of iron (*see* CYANIDES).

FERRIC SALTS.

Are usually of yellowish or reddish brown colour. In solution they are reduced to the ferrous condition by zinc, or, with precipitation of sulphur, by sulphuretted hydrogen. Potassium or other soluble thiocyanate imparts an intense blood-red colour to a neutral or acid solution of a ferric salt.

Ferric fluoride $Fe_2F_6,6H_2O$ *v.* Recoura (Compt. rend. 1912, 154, 655)

Ferric chloride $FeCl_3$ or Fe_2Cl_6 may be obtained in the anhydrous condition by passing excess of chlorine gas over red-hot iron or by passing hydrogen chloride over the heated sesquioxide, and thus occurs not infrequently in the craters of volcanos. Thus prepared, it forms iridescent iron-black scales which are dichroic, appearing red by transmitted and green by reflected light.

In solution it may be prepared by dissolving the precipitated sesquioxide in hydrochloric acid, and driving off the excess of acid by heat; or, preferably, by dissolving iron in hydrochloric acid and passing chlorine through the liquid until saturated with that gas, finally entirely removing the chlorine by passage of a current of carbon dioxide through the warm liquid. A commercial method for the preparation of ferric chloride from native phosphate of iron and aluminium has been described by Schröder (D. R. P. 192591).

Ferric chloride readily volatilises at 448°, and the V.D. is then less than that required for Fe_2Cl_6. It is, therefore, probable that the molecular formula is $FeCl_3$ (Grunewald and V. Meyer, Ber 1888, 21, 687) In boiling alcohol or ether it also appears to have the molecular formula $FeCl_3$ (Muller, Compt. rend. 1894, 118, 641). At the ordinary temperature it forms unstable compounds with nitric oxide, but at higher temperatures it is reduced by that gas to ferrous chloride (Besson, Compt. rend. 1889, 108, 1012; Thomas, *ibid* 1895, 120, 447; 121, 128).

Ferric chloride is very deliquescent, and dissolves in alcohol and ether. The concentrated aqueous solution is dark brown and oily; it diluted it becomes of a pale yellow colour. In dilute solution the salt may exist as $Fe_2Cl_4 \cdot Cl_2$ (Tuferell, Zeitsch. anorg Chem. 1908, 59, 82).

There are four hydrates of ferric chloride, $FeCl_3,6H_2O$, m.p. 37°; $2FeCl_3,7H_2O$, m.p. 32·5°; $2FeCl_3,5H_2O$, m.p. 56°; and $FeCl_3,2H_2O$, m.p. 73·5°. Solutions which contain more of the chloride than corresponds with the composition $FeCl_3,2H_2O$ deposit the anhydrous salt when heated above 66° (Roozeboom, Zeitsch. physikal. Chem. 1892, 10, 477).

Compounds of the formulæ $FeCl_3,HCl,2H_2O$, $FeCl_3,HCl,4H_2O$, and $FeCl_3,HCl,6H_2O$ are known (Sabatier, Bull. Soc. chim. 1881, [ii.] 36, 197; Roozeboom and Schreinemacker, Zeitsch. physikal. Chem. 1894, 15, 588).

Ferric chloride is partly hydrolysed by water with the formation of many complex colloid bodies (Malfitano and Michel, Compt. rend 1907, 145, 185, and 1275; Michel, *ibid.* 1908, 147, 1052, and 1288; Kratz, J. Phys. Chem. 1912, 16, 126).

Ferric chloride forms compounds with alkaloids, most of which have definite melting-points. The use of these substances has been suggested for the identification of the alkaloids (Scholtz, Chem. Soc. Abstr. 1908, i. 202, from Ber. Deut. pharm. Ges. 1908, 18, 44).

Solutions of ferric chloride in methyl alcohol are reduced by light, which acts, not as a catalyst, but as the source of the energy required to bring about the reaction (Benrath, J. pr. Chem. 1909, [ii.] 80, 283).

Ferric chloride is sometimes used as a disinfectant. It deodorises sewage with partial reduction to ferrous chloride.

With potassium chloride it produces a finely crystallised garnet-coloured double chloride $Fe_2Cl_6,4KCl,2H_2O$ decomposed by water. A similar garnet-coloured salt crystallising in cubes is formed with ammonium chloride and is used medicinally as *ammonio-chloride of iron.* The salt used, however, does not correspond to the potassium salt, but usually contains less than 2 p.c. of iron. It is very deliquescent and may be considered as formed by the combination of the normal salt $Fe_2Cl_6,4NH_4Cl,2H_2O$ with variable proportions of ammonium chloride.

Soluble and insoluble *oxychlorides* of iron are known, but are unimportant.

Ferric sulphate $Fe_2(SO_4)_3$ occurs in Chile as *coquimbite* in white silky pyramids containing $Fe_2(SO_4)_3,9H_2O$. It is usually prepared by mixing one equivalent of concentrated sulphuric acid with a solution of two equivalents of ferrous sulphate, concentrated nitric acid being added in portions to the hot solution until red fumes cease to be evolved. On concentrating the solution to a syrup colourless crystals are obtained.

Several hydrated basic sulphates are prepared artificially, or occur in nature.

Ferric sulphate, obtained by dehydrating the hexahydrate at 108°, dissolves in ethyl alcohol to form a solution in which barium chloride forms no precipitate of barium sulphate. This fact is explained by Recoura (Compt. rend. 1911, 153, 1223) by assuming that the trihydrate has the constitution $Fe_2(SO_3)_3(OH)_6$ analogous to the green pentahydrate of chromic sulphate.

Ferric sulphate is used to a slight extent in dyeing cotton, but not in printing. The basic sulphates are used for dyeing cotton, for the production of buffs, or, in combination with logwood and sumach, for blacks. The iron mordant prepared by treating ferrous sulphate with nitric acid is sold as *nitrosulphate* or *nitrate of iron*, and is used in dyeing, but not in printing cotton.

With alkaline sulphates ferric sulphate forms double salts, resembling and corresponding in composition to alum.

The potassium salt, *potassium iron alum* $Fe_2(SO_4)_3,K_2SO_4,24H_2O$, is prepared by mixing molecular proportions of ferric and potassium sulphates and concentrating the solution spontaneously. It forms fine violet octahedra very liable to decompose into a brown, gummy, deliquescent mass. This alum is used to a limited extent in dyeing and calico-printing. If caustic potash is added to a solution of iron alum, and the brown liquid allowed to evaporate, yellowish-brown crystals separate of the composition $5K_2SO_4, 2Fe(SO_4)_2(OH)_2,16H_2O$. These crystals have the peculiar optical properties of tourmaline (*see* Lachaud and Lepierre, Compt. rend. 1892, 114, 915).

The corresponding ammonium alum is more permanent, and has been proposed as a standard in titrations (de Coninck, Bull. Soc. chim. 1909, 23, 222).

Ferric nitrate $Fe_2(NO_3)_6$ may be obtained in several states of hydration by crystallising the solution obtained by the action of concentrated nitric acid on scrap iron or iron oxide. The hydrate $Fe_2(NO_3)_3,6H_2O$ crystallises in cubes and the hydrate $Fe_2(NO_3)_3,9H_2O$ in colourless monoclinic crystals. It is usually prepared by the first method for use as a mordant for producing buffs and blacks in dyeing. An alkaline mordant is prepared for dyeing and calico-printing by treating a ferric salt with caustic soda, with addition preferably of glycerol, or sometimes of glucose, to prevent precipitation of the oxide.

Nitroso-compounds of Iron. Anhydrous ferric chloride absorbs nitric oxide, forming the compounds $2FeCl_3{\cdot}NO$ and $4FeCl_3{\cdot}NO$ as reddish-brown, hygroscopic powders. The action of nitric oxide on an ethereal solution of ferric chloride gives nitrosyl chloride and a solution which, when evaporated over sulphuric acid, deposits black needles of the composition $FeCl_3{\cdot}NO,2H_2O$; or at 60° gives the anhydrous salt $FeCl_3NO$, crystallising in yellow needles (Thomas, Compt. rend. 1895, 120, 447).

The stable nitroso compounds were discovered by Roussin (Compt. rend. 1858, 46, 224), and are formed by the action of ferrous sulphate on alkali nitrites and sulphides. They are salts of complex acids, containing iron and the monovalent group NO′ in the acid radicle (Cambi, Atti. R. Accad. Lincei. 1908, [v.] 17, i. 202), and fall into two classes:

(1) *Ferrodinitroso* derivatives.

(2) *Ferroheptanitroso* derivatives.

Potassium ferrodinitroso sulphide

$$K[Fe(NO)_2S],2H_2O$$

is formed by the action of caustic potash on the heptanitrososulphide (*v. infra*). It forms dark red crystals, insoluble in water, and decomposes violently when heated, yielding potassium and ammonium sulphates and other products.

The free acid $H[Fe(NO)_2S]$ is obtained by the action of sulphuric acid on the potassium salt and slowly decomposes into hydrogen sulphide, nitrogen, nitrous oxide, and the heptanitroso acid. The ethyl and phenyl derivatives have been prepared: $C_2H_5[Fe(NO)_2S]$, and

$$C_6H_5[Fe(NO)_2S].$$

Potassium ferrodinitrosothiosulphate

$$K[Fe(NO)_2S_2O_3],H_2O$$

is prepared by passing nitric oxide into a solution of ferrous sulphate and potassium thiosulphate for 10 hours. It forms reddish-brown crystals with a bronze lustre which are but slightly soluble in water. The ammonium and sodium salts are similar, but the latter is the more soluble.

Potassium ferroheptanitrososulphide

$$K[Fe_4(NO)_7S_3],H_2O$$

is the most stable of these salts and is formed by the action of ferrous sulphate on potassium nitrite and sulphide in solution, or by boiling a solution of the ferrodinitrosothiosulphate. It forms dark-coloured monoclinic crystals having an adamantine lustre and is only sparingly soluble in water.

The free acid is obtained as an amorphous brown mass by the action of sulphuric acid on the potassium salt.

The ammonium salt may be prepared by the action of nitric oxide on freshly precipitated ferrous sulphide suspended in water.

(For details as to these compounds *see*: Proczinsky, Annalen, 1863, 125, 302; Rosenberg, Ber. 1870, 3, 312; Pavel, *ibid.* 1882, 15, 2600; Marchlewski and Sachs, Zeitsch. anorg. Chem. 1892, 2, 175; Marié and Marquis, Compt. rend. 1896, 122, 137; Hofmann and Wiede, Zeitsch. anorg. Chem. 1895, 8, 318; 1895, 9, 295; 1895, 11, 281; *see* also Atti. R. Accad. Lincei, 1906, [v.] 15, ii. 467; 1907, [v.] 16, i. 654.)

Ferric phosphates occur native as *beraunite*

$$Fe_2(PO_4)_2{\cdot}4Fe_2PO_4(HO)_3,8H_2O,$$

formed by the oxidation of *vivianite*, and as *dufrenite* $Fe_2(HO)_3PO_4$.

The normal phosphate, $FePO_4$, is produced as a yellowish-white precipitate by adding sodium hydrogen phosphate to ferric chloride solution; it is soluble in dilute acids (except acetic acid) and is slowly decomposed by water.

When ferric hydroxide is dissolved in orthophosphoric acid and the solution rapidly evaporated, the di-acid salt $Fe(H_2PO_4)_3$ is obtained as a pink crystalline powder, decomposed by moist air, with formation of the monacid salt $2FeH_3(PO_4)_2,5H_2O$.

Ferric metaphosphate is deposited in pink plates when the hydroxide is digested with glacial phosphoric acid at 100° (Hautefeuille and Margotte, Compt. rend. 1888, 106, 138; Johnson, Ber. 1889, 22, 976).

Pascal has described (Compt. rend. 1908, 146, 231, 279) certain complex salts of iron with phosphoric acid in which the iron exists in the acid radicle.

Sodium ferripyrophosphate $Na_6Fe_2(P_2O_7)_3$ is precipitated as a pale violet, micro-crystalline powder from a saturated solution of ferric pyrophosphate in 15 p.c. sodium pyrophosphate solution maintained at 30°. The silver and copper salts and the free acid have been prepared.

Ferric arsenite $Fe_2(AsO_3)_2$ is of interest as being the salt produced when freshly precipitated hydrated oxide of iron is taken as an antidote in cases of arsenical poisoning. It may be obtained as a brown precipitate by addition of arsenious acid or an arsenite to a solution of ferric acetate.

Ferric acetate *v.* Acetates.

Ferric ferrocyanide *v.* Cyanides.

Ferric tannate or *gallo tannate* forms the basis of black inks (*v.* Ink). The sponges, sand, pumice-stone, &c., of Gerson's filters are impregnated with the tannate, which is said to completely remove all organic matter from water (*v.* Steiger, J. Soc. Chem. Ind. 1886, 416).

Ferric citrate $Fe(C_6H_5O_7)$ is prepared by dissolving the hydrated oxide in citric acid, and evaporating the solution in thin layers. It forms permanent, transparent, garnet-coloured scales, which dissolve slowly in water, but are insoluble in alcohol.

Ferric ammonium citrate is prepared as above, with addition of ammonia. It forms thin, transparent, deep-red scales, which dissolve readily in water, but not in absolute alcohol.

It is used in medicine as is also the double citrate of iron and quinine.

IRON CARBONYLS. Three carbonyls of iron are known, viz.: Iron pentacarbonyl $Fe(CO)_5$, iron tetracarbonyl $Fe(CO)_4$, and diferrononacarbonyl $Fe_2(CO)_9$.

Iron pentacarbonyl. This compound was discovered by Mond, Langer, and Quincke, who prepared it by treating finely divided iron, obtained by reducing ferrous oxalate by hydrogen, with carbon monoxide. On heating to 120°, the carbonyl distilled over and was collected in a cooled tube. The yield is about 1 gram per 100 grams of iron (Chem. Soc. Trans. 1891, 604 and 1090).

Iron pentacarbonyl is a viscid yellow liquid of sp.gr. 1·466 at 18°; b.p. 102·8° at 749 mm. At −21° yellow crystals are formed, which become white at the temperature of liquid air.

It is not acted upon by dilute acids, but concentrated acids form the corresponding salt with evolution of carbon monoxide and hydrogen. Upon exposure to air, it is converted into ferrous hydroxide and eventually into the red ferric hydroxide. The pentacarbonyl is soluble in most organic solvents and in nickel tetracarbonyl, forming $FeNi(CO)_9$ (?), insoluble in water.

Light decomposes the pentacarbonyl, giving the diferrononacarbonyl and carbon monoxide: $2Fe(CO)_5 = Fe_2(CO)_9 + CO$ (Dewar and Jones, Proc. Roy. Soc. 1905, A. 76, 588; 1907, A. 79, 66).

The decomposition of the pentacarbonyl is most rapid in blue light and least of all in red, green and yellow being intermediate in their effects; in fact, a solution exposed to blue light will deposit about ten times as much solid as a similar solution exposed for the same period to red light.

The action of light on the pentacarbonyl is reversible, as the substance in sealed tubes, after exposure to light, when left in the dark, gradually become colourless.

Diferrononacarbonyl crystallises in lustrous hexagonal golden or orange-coloured crystals of sp.gr. 2·085 at 18°, which are perfectly stable in dry air. They are decomposed at 100° yielding the pentacarbonyl, carbon monoxide, and iron: $Fe_2(CO)_9 = Fe(CO)_5 + 4CO + Fe$. It is insoluble in water and nearly so in benzene, but is slightly soluble in alcohol or acetone and very soluble in pyridine. The nonacarbonyl in solution heated to 95° becomes green and then contains the *tetracarbonyl* $Fe(CO)_4$. At a higher temperature it forms the pentacarbonyl together with iron and carbon monoxide, the reaction taking place in two stages:

$$2Fe_2(CO)_9 = 2Fe(CO)_5 + 2Fe(CO)_4$$
$$2Fe(CO)_4 = Fe(CO)_5 + Fe + 3CO$$

When strongly heated the action is:

$$2Fe_2(CO)_9 = 3Fe(CO)_5 + Fe + 3CO$$

Iron tetracarbonyl. The method of preparation of the tetracarbonyl is as follows: a solution of the diferrononacarbonyl in toluene (1 gram to 20 c.c.) is gradually heated to 95° in an atmosphere of carbon dioxide until the reddish-yellow solid has disappeared. On cooling, green crystals of the tetracarbonyl are formed:

$$Fe_2(CO)_9 = Fe(CO)_4 + Fe(CO)_5$$

The yield is 20 p.c.

The tetracarbonyl forms dark green lustrous crystals of sp.gr. 1·996 at 18°, stable at ordinary temperatures: on heating at 140°–150°, iron and carbon monoxide are formed. The empirical formula is $Fe(CO)_4$, but the molecular formula in benzene appears to be $[Fe(CO)_4]_{20}$.

The substance is insoluble in water but soluble in most organic solvents giving green solutions. In pyridine, the solutions are first green, but soon become red, especially on warming. The change in colour is probably due to molecular dissociation. The green solutions lose their colour upon exposure to light, iron being deposited, but the red ones are unaffected by light.

IRON CEMENT *v.* Lutes.

IRON LIQUOR. *Ferrous acetate* (*v* Acetic acid).

IRON PYRITES. *Ferric sulphide* (*v.* PYRITES; IRON).

IRONE *v.* KETONES.

IRVINGIA BUTTER *v.* WAXES.

ISATIN *v.* BONE-OIL; INDIGO, NATURAL; INDIGO, ARTIFICIAL.

ISATIN BLUE *v.* BONE-OIL.

ISETHIONIC ACID $CH_2OH\cdot CH_2SO_3H$, an isomeride of ethyl sulphuric acid obtained by the action of sulphur trioxide on ethlylene, or ethyl alcohol. Has the dual function of a sulphonic acid and alcohol. With phosphorus pentachloride forms the chloro-acid chloride $CH_2Cl\cdot CH_2SO_2Cl$, which on hydrolysis yields *chloroethyl sulphonic acid* $CH_2Cl\cdot CH_2SO_3H$. This heated with ammonia solution forms amino ethyl sulphonic acid $CH_2NH_2\cdot CH_2SO_3H$, which is the *taurine* of bile. (*V.* art. TAURINE.)

ISINGLASS (Fr. *Colle de poisson*; Ger. *Hausenblase*) consists of the dried swimming-bladders of various fishes. These bladders differ in shape and size, according to their origin, and are prepared either by simply drying them whilst slightly distended, which process forms 'pipe isinglass,' or by splitting them open, pressing, and drying them in the form of 'leaf isinglass.' That form, again, which is known as 'purse isinglass,' consists of such bladders as contain a natural opening.

The chief supply of isinglass is derived from Russia and Hudson's Bay; some portion also being obtained from Brazil, West Indies, Penang, Bombay, and Manilla; the finest kind, the 'Beluga leaf,' coming from the first-named of these countries, and being the produce of a species of sturgeon. Other Russian or Siberian varieties are 'Astrakhan leaf,' 'Saliansky leaf,' and 'Samovy leaf.'

The following are the principal species of fish from which Russian isinglass is obtained: *Acipenser huso*, or the Hausen; *A. Guldenstædtii*, or the Osseter; *A. ruthenus*, or the Sterlet; *A. stellatus*, or the Sewruga; *Silurus glanis* and *Cyprinus carpio*. The isinglass of New York is derived from *Labrus squeteague*; that of New England—the 'ribbon isinglass'—from the common Cod, *Gadus Morrhua*. In Brazil, it is taken from a species of *Silurus*; and in Iceland, from *Gadus* and *Molva vulgaris*, or the Ling.

The chief emporium for Russian isinglass was the great fair of Nijni-Novgorod, whence the largest part of the merchandise found its way to London, through the agency of Petrograd traders. It arrived here about the end of June. Those supplies which reach us from Brazil and other countries are received at all seasons.

The fish being taken, the bladders are immediately removed, sufficient care in the cleansing of them from mucus and blood-stains being often purposely neglected, since a loss of weight results in the process when properly performed. In consequence of this neglect, the value of the material is diminished in proportion to the impurities which it contains.

On its arrival here isinglass is a hard, tough substance, and for many purposes it is necessary to 'cut' it. The operations of 'cutting' consist, first, in soaking the flakes until somewhat pliable, trimming the edges, and scraping off the dark spots; next, in putting them through two sets of rollers, under great pressure, by which they are flattened to the thickness of writing-paper; and, finally, in cutting them into fibres of extreme fineness, a process now almost always effected by a machine constructed for that purpose.

The uses for which isinglass is employed are the 'fining' or clarifying of fermented beverages, as ale and wine, and various culinary preparations. For the former purpose, the properties of isinglass are remarkable; for, whilst possessing the exact chemical composition of gelatin, it has the power, which is wanting in gelatin, of entangling in the film or web which it forms as it dissolves, all the suspended impurities contained in the liquids which it is sought to clarify. The lower grades of isinglass are used either in the natural or the manufactured condition by brewers and the manufacturers of cider, and the better classes of the Russian material by wine merchants. For the purpose of the brewer it is usual to dissolve the isinglass in sulphurous acid which has a tendency to preserve the ale.

The choicest descriptions are used by the cook and the confectioner for the thickening of soups, jellies, &c., but as for these purposes the fining properties of isinglass are not of any account, gelatin serves equally well, and has, under the name of patent isinglass, been so employed (*v.* GLUE).

ISOCETIC ACID $C_{14}H_{29}COOH$, m.p. 55°, is obtained from the oil extracted from the seeds of *Jatropha Curcas* (Linn.) (Bouis, J. 1854, 462).

ISOFORM *v.* SYNTHETIC DRUGS AND IODOFORM.

ISOPRAL. *Trichloroisopropyl alcohol*

$$CCl_3\cdot CHOH\cdot CH_3$$

m.p. 49°. Obtained by the action of methyl magnesium bromide on chloral. Used as a hypnotic (*v.* SYNTHETIC DRUGS).

ISOPRENE. *β-Methyldivinyl*

$$CH_2 : C(CH_3)CH : CH_2$$

Discovered by Greville Williams among the products obtained by the destructive distillation of rubber (Phil. Trans. 1860, 241). Tilden obtained it among the more volatile compounds obtained by the action of heat on oil of turpentine and other terpenes (Chem. Soc. Trans. 1879, 417; 1884, 415), and Gladstone from refraction and dispersion measurements came to the same conclusion as Tilden, viz. that the so-called *pentine* obtained from turpentine was identical with isoprene from rubber (Chem. Soc. Trans. 1896, 619). Mokiewski (J. Russ. Phys. Chem. Soc. 1898, 30, 885) found that isoprene obtained from turpentine contains some trimethylethylene, for on treatment with one molecule of bromine in a cooled ethereal solution, isoprene dibromide and any amylene derivative were obtained. Ipatiew and Wittorf (J. pr. Chem. 1897, [ii.] 55, 1) proved the presence of trimethylethylene in isoprene obtained from rubber. By treating isoprene dibromide with zinc-dust, pure isoprene is obtained. Staudinger and Klever (Ber. 1911, 44, 2212), using Tilden's method, have shown that a better yield of isoprene can be obtained by working under reduced pressure. A 60 p.c. yield of isoprene can be obtained by passing the vapours of dipentene or limonene under very greatly reduced pressure over an electrically heated platinum spiral: the isoprene so obtained is almost pure, containing very little trimethylethylene. Terpineol, terpinene and camphene do not yield isoprene under these conditions.

Harries and Gottlob (Annalen, 1911, 383, 228) have described an 'isoprene lamp' (Fig. 1) for the production of the hydrocarbon from turpentine and limonene by this process (Harries, D. R. PP. 243075, 243076).

A platinum wire (120 cm. long, resistance at medium red heat 9 ohms, taking 5 amps at 220 volts) is heated to redness above the surface of the boiling liquid. A reflux condenser, through which circulates water at 50°, is attached to the flask. The isoprene is collected by a side tube leading to a vessel cooled in a freezing mixture. The product is rectified through a column and the fraction 35°-37° is separated. Commercial pinene in this way gives about 1 p.c. of isoprene, whilst carvene gives 30-50 p.c. according to the amount of limonene present.

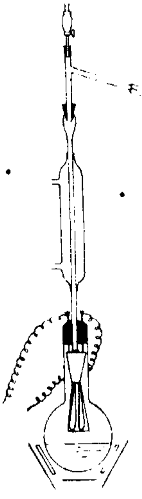


FIG. 1

Methyl*iso*propenyl carbinol

$$\mathrm{CH_2 : CMe\cdot CHMe\cdot OH}$$

heated to 130°–150° with anhydrous oxalic acid, zinc chloride, hydrogen potassium sulphate, or other similar dehydrating agent, yields isoprene (Bayer & Co., D. R. P. 246241). *as*-Dimethylallene (b.p. 39°–41°), dropped on to strongly heated alumina under a pressure of about 20-30 mm. is converted into isoprene (Badische Anilin- & Soda-Fabrik, D. R. P. 251216). *See* also D. R. P. 231806 for the exhaustive methylation of αδ-diaminobutane and its derivatives.

Euler (Ber. 1897, 30, 1989) has obtained isoprene by the exhaustive methylation of β-methyl pyrrolidine, a reaction which establishes its structure, as does Ipatiew's synthesis from dimethylallene (J. pr. Chem. 1897, [ii.] 55, 1, 4). The latter hydrocarbon by the addition of hydrogen bromide yields β-methyl-βδ-dibromobutane, which on treatment with alcoholic potash is converted into isoprene.

$$\mathrm{(CH_3)_2C : C : CH_2 \rightarrow (CH_3)_2CBr\cdot CH_2\cdot CH_2\cdot Br}$$
$$\mathrm{\rightarrow CH_3\cdot C(: CH_2)\cdot CH : CH_2}$$

Harries (Ann. 1911, 383, 157) has also prepared the hydrocarbon from acetone. In this series of reactions the ketone is converted by the action of magnesium ethyl iodide into dimethyl ethyl carbinol, elimination of water from this alcohol transforming it into trimethyl ethylene. Addition of bromine to the ethylene hydrocarbon yields β-methyl-βγ-dibromobutane, which when passed over hot soda lime decomposes into hydrogen bromide and isoprene.

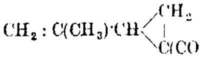
$$\mathrm{(CH_3)_2CO \rightarrow (CH_3)_2C(C_2H_5)\cdot OH}$$
$$\mathrm{\rightarrow (CH_3)_2C{=}CH\cdot CH_3}$$
$$\downarrow$$
$$\mathrm{CH_3\cdot C(: CH_2)\cdot CH : CH_2 \leftarrow (CH_3)_2CBr\cdot CHBr\cdot CH_3}$$

W. H. Perkin and his collaborators (J. Soc. Chem. Ind. 1912, 31, 616) have devised a method for the preparation of isoprene from commercial fusel oil. The fraction of fusel oil, boiling at 128°-130°C. (consisting mainly of isoamyl alcohol, together with some active amyl alcohol), is subjected to the action of dry hydrogen chloride and then further chlorinated in a specially constructed apparatus. On distillation the product was found to consist of γδ-dichloro-, βγ-dichloro-, and αδ-dichloro-β-methyl butanes. These products were not separated, but the combined fraction (b.p. 140°–180°) was passed over soda lime at 470° and the vapour condensed. On fractionation of the product a 40 p.c. yield of isoprene was obtained. It would seem that in this process the γδ-dichloro-β-methyl butane must first yield an isopropyl acetylene which then undergoes molecular rearrangement into isoprene

$$\mathrm{(CH_3)_2CH\cdot CHCl\cdot CH_2Cl \rightarrow (CH_3)_2CH\cdot C : CH}$$
$$\mathrm{\rightarrow CH_3\cdot C(: CH_2)\cdot CH : CH_2}$$

Isoprene is a colourless liquid, b.p. 33·5° (Mokiewski; Ipatiew, *l.c.*); sp.gr. 0°/0° 0·6989 (M. *l.c.*); magnetic rotation, 7·529; sp.gr. 15°/15°, (from turpentine) 0·6768, (from rubber) 0·6748 (Perkin, Chem. Soc. Trans. 1895, 258); thermal expansion (Thorpe and Jones, *ibid.* 1893, 277). For a redetermination of the physical constants, *see* Harries, Ber. 1914, 47, 1999. By heating isoprene to 300°, only a little dipentene is formed, but a quantity of another hydrocarbon (b.p. 64°-66° (12 mm.)), possibly diisoprene, and also di- and polymyrcene (*v.* RUBBER) (Harries, Ber. 1902, 3265; Tilden, Chem. News, 46, 120; Bouchardt, Compt. rend. 87, 654; 89, 361). According to Bouchardt (*l.c.*) and Tilden (Chem. News, 1892, 65, 265), strong acids, such as hydrochloric acid, convert isoprene into a tough elastic substance resembling rubber. Bourchardt (Gummi-Zeit, 1901, 16, [viii.] 133) finds that when isoprene (1 part) and hydrochloric acid (12–15 parts) saturated at 0° are sealed in a tube and placed in a freezing mixture, much heat is evolved on shaking. After leaving for 2 or 3 weeks, the contents were diluted and distilled until oily drops ceased coming over. The residue was purified by boiling with water, had all the properties of rubber and gave similar distillation products. Analysis gave the following figures: C=87·1; H=11·7; Cl=1·7. Tilden found that on standing for some months, isoprene is slowly polymerised into a rubber-like substance. Harries (Chem. Zeit. 1910, 34, 315) converted isoprene into rubber by means of acetic acid, but could not effect the change with hydrochloric acid. Chromic acid oxidises isoprene into carbon dioxide, formic, and acetic acids; nitric acid yields oxalic acid. Isoprene dibromide $\mathrm{CH_2 : C(CH_3)CHBr\cdot CH_2Br}$ is formed when isoprene is treated with bromine in carbon disulphide solution at 0° (Blaise and Courtot, Bull. Soc. chim. [iii.] 35, 989); b.p. 101° (19 mm.).

On treatment with sodium ethoxide and ethyl malonate, it yields an ethyl ester $C_{12}H_{18}O_4$, which on hydrolysis yields isopronic acid (*iso*propyltrimethylenedicarboxylic acid)



$$CH_2:C(CH_3)\cdot CH\left\langle\begin{array}{l}CH_2\\ |\\ C(CO_2H)_2\end{array}\right.$$

m.p. 115° (Ipatiew, J. Russ. Phys. Chem. Soc. 1901, 33, 540). Ostromisslenski and Koscheler (J. Russ. Phys. Chem. Soc 1913, 47, 1928) have shown that isoprene undergoes auto-condensation when preserved at 80°-90°, yielding the open chain dimerile β-myrcene

$$CH_2:C(CH_3)\cdot CH_2\cdot CH_2\cdot CH:C(CH_3)\cdot CH:CH_2$$

ISOTONIC SOLUTIONS. Solutions having the same osmotic pressure.

ISPAGHULA (B.P). The dried seeds of *Plantago ovata* (Forsk.).

ISTIZIN. Trade name for 1·8-dihydroxyanthraquinone.

ITROL v. SYNTHETIC DRUGS.

IVORY is essentially *dentine*, the main constituent of all teeth, but usage restricts the term to the dentine of those teeth which are available for industrial purposes; chiefly those of the elephant, hippopotamus, walrus, narwhal, and sperm-whale.

Ivory contains 57–60 p.c. of calcium salts, chiefly the phosphate, with 40–43 p.c of an organic matrix and 0·24–0·34 p.c. of fat. It differs from other dentines chiefly in the large amount of organic matter it contains (*cp.* human dentine containing 25 p.c. of organic matter), and in its structure (*v. infra*) and from bone in its greater elasticity and the absence of the larger canals conveying blood vessels.

The substance of ivory is permeated by an immense number of fine canals, about $\frac{1}{1500}$ inch in diameter and strongly curved, to which are due its fineness of grain and probably much of its elasticity. That obtained from the tusks of *Proboscidea* exhibits, on a transverse section, a characteristic pattern of curved decussating lines. The cross-section shows a central spot, the residue of the pulp-centre (*v. infra*), surrounded by concentric circular 'contour lines,' due to a number of minute, irregular 'interglobular spaces.' These spaces and the canals are probably filled with protoplasmic matter in the living tooth. The exterior of the tooth is covered with cementum, usually of a brown colour.

Most of the ivory now used is obtained from the upper incisor teeth of the elephant. The tusks of the African elephant are 9–10 feet long and weigh up to 160 lbs., and are possessed by both males and females. Of Indian elephants, none of the females and not all the males have tusks, and those of the latter are usually less than 8 feet in length and 90 lbs. weight. Captive elephants have their tusks shortened and the ends bound with metal. The tusks grow continuously, and if cut at intervals of ten years yield a useful amount of ivory, although that from wild elephants, especially African elephants, is more highly valued.

The tusks are implanted to the extent of about half their length in curved bony sockets which run nearly vertically upwards to the level of the eyes. The part within the socket has a conical centre of pulp by the conversion of which into dentine growth takes place, fresh pulp being continually formed at the base of the tooth. The pulp is not easily injured and sometimes foreign bodies, such as bullets and spear-heads, have been found embedded in solid ivory, their presence in the pulp having failed to inhibit its conversion into dentine.

In Russia the tusks of mammoths from North Siberia are much used; they have been preserved unchanged from prehistoric times by the low temperatures of that region.

The canine teeth of the hippopotamus yield an ivory harder and whiter than that of the elephant, and less prone to turn yellow.

Among Northern nations, the upper canine teeth of the walrus are used as a source of ivory. They consist of dentine covered with cementum and have an axis of secondary dentine which is nodular in appearance but usually dense and uniform. The spiral tusk of the narwhal is similarly employed.

Ivory is largely used for making billiard balls, graduated scales, knife-handles, piano-keys, combs, fans, &c., and a considerable quantity is imported into China for the manufacture of ornamented articles. Dieppe is the principal centre for ivory-working in Europe.

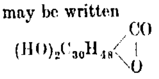
As ivory shrinks when dried it is usually cut roughly to shape first, then dried spontaneously or by heat, and finally finished. Because of its high price, great care is taken to cut it up economically and all chips, cuttings, &c., are used for making *ivory-black* or for the preparation of a very pure gelatin.

Ivory can be made flexible by treatment with phosphoric acid and re-hardened by washing and drying, but not without injury to its quality. It takes dyes well and it may be bleached by exposure to sunlight and moisture, by the action of hydrogen peroxide, or by washing alternately with solutions of potassium permanganate and of oxalic acid (Textile Colourist, 1901, 23, 285; *v.* also Livache, J. Soc. Chem. Ind. 1903, 307).

IVY. The leaves, berries, and wood of the common ivy, *Hedera Helix* (L.) have been used in medicine; they contain a mixture of glucosides, soluble and insoluble in water. One of the latter is crystalline, and has been repeatedly examined, last and most thoroughly by van der Haar (Pharm. Weekblad, 1913, 50, 1350, 1381, 1413; *see* also Arch. Pharm. 1912, 250, 424). This author calls it *α-hederin*; m.p. 256°–257°, $[\alpha]_D^{10°}$ +9·68° in alcohol. The formula is possibly $C_{42}H_{66}O_{11},2H_2O$. It forms small colourless needles, soluble in concentrated sulphuric acid with an orange colour, becoming bright red and finally colourless, as a violet precipitate deposits. It forms a penta-acetyl derivative, m.p. about 155°, and contains one methoxy group. It does not foam on shaking with water. It is hydrolysed slowly by boiling 4 p.c. sulphuric acid to α-hederagenin, arabinose, and rhamnose, probably according to the equation

$$C_{42}H_{66}O_{11}+3H_2O=C_{31}H_{50}O_4+C_5H_{10}O_5+C_6H_{12}O_3$$

α-Hederagenin $C_{31}H_{30}O_4$, m.p. 325°–326°, forms rhombic prisms, and has $[\alpha]_D^{20}$ + 81·2° in pyridine. It may be written



$$(HO)_2C_{30}H_{48}\left\langle\begin{array}{l}CO\\ |\\ O\end{array}\right.$$

as it contains a lactone group, but no methoxy-group, and yields a diacetyl derivative (m.p. 110°). On distillation with zinc-dust a greenish fluorescent oil is obtained, containing a *sesquiterpene*, $C_{15}H_{24}$, which still gives the same violet-red coloration as hederagenin, and as the original glucoside. The portion non-volatile with steam is probably $(C_5H_8)x$.

There seems little doubt that this glucoside is identical with the *hederin* of Houdas (Compt. rend. 128, 1463) ($C_{64}H_{104}O_{19}$, m.p. 248°), which on hydrolysis gave *hederedin*, $C_{26}H_{40}O_4$, m.p. 324°, rhamnose and hederose (= arabinose ?), and it may further be the same as the *ivy glucoside* $C_{32}H_{54}O_{11}$,$2H_2O$, m.p. 233°, isolated by earlier investigators from the leaves, but mostly from the berries (Davies and Hutchinson, Pharm. J. [iii.] 7, 275; Davies, *ibid.* [iii.] 8, 205; Kingzett, *ibid.* [iii.] 8, 206; Vernet, J. 1881, 91; Vincent, Bull. Soc. chim. 35, 231; Block, Arch. Pharm. [iii.] 26, 953). The leaves may be exhausted with hot water and then with hot 90 p.c. alcohol, or the berries may be exhausted with ether, and then with alcohol. The alcoholic extract is treated with charcoal, or, after evaporation, washed with cold benzene, and then dissolved in hot alcohol or acetone, when on cooling and concentration the glucoside crystallises. (Houdas's hederin dissolved in 54 parts of alcohol at 18° and in 0·22 parts at 78°.) Ivy glucoside gives a violet colour reaction with sulphuric acid like that described above, and is stated by Block to be hydrolysed to a substance $C_{20}H_{42}O_6$ (?), m.p. 280°, and a sugar.

Posselt has described amorphous hederotannic acid and hederic acid from the berries (Annalen, 69, 62).

The physiological action of ivy glucosides has been examined by Joanin (Compt. rend. 128, 1476), and by Moore (J. Pharm. exp. Therap. 1913, 4, 263).

A peroxydase from ivy has been prepared in a purified condition by van der Haar (Ber. 1910, 43, 1327), who regards it as a gluco protein.

For ivy gum resin, *see* GUM RESINS. G. B.

J

JABORANDI AND ITS ALKALOIDS. The leaves of *Pilorarpus Jaborandi* (Holmes) were introduced into European medicine by Coutinho and Gubler in 1874 (Rep. de Pharm. 2, 171) under the name 'jaborandi,' which has since been employed generally for the leaves of various species of pilocarpus indigeneus to the eastern parts of S. America. *Pilocarpus Jaborandi* (Pernambuco Jaborandi) is no longer obtainable in quantity, the Jaborandi of commerce being usually the leaves of *P. microphyllus* (Stapf.) (Maranham Jaborandi), although the leaves of *P. pennatifolius* (Lem.), *P. racemosus* (Vahl.), *P. spicatus* (A. St. Hill), and *P. trachylophus* (Holmes) have also appeared in trade.

The leaves of *P. Jaborandi* were official in the B.P. 1898, but have been omitted from the B.P. 1914. In the U.S.P. these leaves and those of *P. microphyllus* are official. Owing to the fact that the sole physiological activity of the leaves has been shown to be due to the pilocarpine they contain (Jowett and Marshall, British Medical Journal, 13th Oct. 1900), and to the greater convenience attained by the use of the salts of this alkaloid, the employment of the galenical preparations of Jaborandi has practically ceased and they are no longer used to any appreciable extent in medicine. No preparation of the drug is recognised in the B.P. and the fluid extract only in the U.S.P., but galenical preparations of Jaborandi have been used as an ingredient in hair washes and restorers. Of the salts of pilocarpine, the nitrate is usually employed in Great Britain, being stable and sufficiently soluble in water for practical purposes; though the hydrochloride, which is more soluble in water, but deliquescent in the air, is preferred on the Continent of Europe and America. The drug was examined by Hardy (Bull. Soc. chim. 1875, [ii.] 24, 497), Gerrard (Pharm. J. 1875, [iii.] 5, 865, 965; 1877, [iii.] 7, 225), Harnack and Meyer (Annalen, 1880, 204, 67), Jowett (Chem. Soc. Trans. 1900, 77, 474, 851; 1901, 79, 581, 1331), Jowett and Pyman (Chem. Soc. Proc. 1912, 28, 268), and Pyman (Chem. Soc. Trans. 1912, 101, 2260; *cf.* Léger and Roques, Compt. rend. 1912, 155, 1088; 1913, 156, 1687). The results of these researches show that *P. microphyllus* leaves contain pilocarpine, *iso*-pilocarpine (β-pilocarpine of Brühl, Hjelt, and Aschan; pilocarpidine of Petit and Polonowsky (J. Pharm. Chim. 1897, [vi.] 5, 370, 430, 475; 1898, 6, 8), and pilosine. Harnack and Meyer's pilocarpidine (Chem. Zeit. 1885, 628) and jaborine (Annalen, 1880, 204, 67) may occur in *P. Jaborandi* leaves, which are no longer obtainable in commerce. A sample of jaborine obtained from Merck and examined by Jowett (Chem. Soc. Trans. 1900, 77, 492) proved to consist of a mixture of *iso*pilocarpine, pilocarpidine, and possibly pilocarpine, with non-alkaloidal substances. Petit and Polonowsky have stated that *P. spicatus* leaves contain ψ-pilocarpine and ψ-jaborine (*l.c.*). Pilocarpine, *iso*pilocarpine, and pilocarpidine produce similar effects on the secretory activity of the sweat and salivary glands, though pilocarpine is much the most powerful, and they also cause contraction of the pupil of the eye, and in this respect are antagonistic to atropine.

Preparation of the alkaloids.—These alkaloids are characterised by being soluble in water and in chloroform, and in being remarkably stable to acids and alkalis (except that pilocarpine on heating for a long time or on long contact with the fixed alkalis becomes converted into *iso*pilocarpine). The general methods of the extraction of alkaloids modified to suit these properties can be successfully employed. The usual procedure is as follows :—

The finely powdered leaves are extracted with alcohol containing hydrochloric acid. The solvent is distilled off, the aqueous residue filtered, neutralised with ammonia, and evaporated to a low bulk. Excess of ammonia is then added and the alkaloids extracted with chloroform. The chloroform is distilled off, the residue dissolved in as little water as possible, and neutralised with dilute nitric acid. The crystalline nitrates which form are separated into pilocarpine nitrate and *iso*pilocarpine nitrate by recrystallisation from alcohol until each is of constant melting-point.

Estimation.—A weighed quantity of the finely powdered drug is extracted in a Soxhlet apparatus with alcohol containing 1 p.c. of ammonia. The alcohol is distilled off and the residue dissolved in water, made alkaline with ammonia if necessary, and extracted with chloroform. The chloroform solution is separated, the solvent distilled off, and the residue dried at 100° and weighed. It represents the total alkaloids. Jowett (Pharm. J. 1899, [iv.] 9, 91) has proposed a method for the approximate estimation of pilocarpine in this residue by conversion into the crystalline nitrate and observation of the optical rotation of the product. Of the important varieties of Jaborandi leaves met in commerce, the most common *P. microphyllus* (Stapf.), contains from 0·75 p.c. to as much as 1 p.c. of total alkaloid of which about 75 p.c. is pilocarpine, whilst *P. Jaborandi* (Holmes) contains about 0·72 p.c., of which 93 p.c. is pilocarpine (Paul and Cownley, Pharm. J. 1896, [iv.] 3, 1).

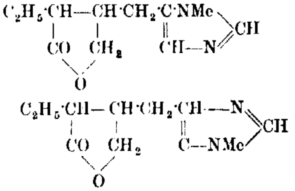
Pilocarpine $C_{11}H_{16}O_2N_2$ is a colourless oil, soluble in water, alcohol, or chloroform, b.p. 260° under 5 mm. pressure, being partially converted into *iso*pilocarpine (*see* below) in the process. Dextrorotatory, $[\alpha]_D +100{\cdot}5°$; the rotation is reduced by the addition of alkali. The salts crystallise well; the nitrate $B{\cdot}HNO_3$ forms well-defined prisms, m.p. 178°; the hydrochloride B·HCl white deliquescent crystals, m.p. 204°–205°; the aurichloride $B{\cdot}HAuCl_4$, lemon-yellow needles, m.p. 117°–130° (dry); and the picrate, characteristic long needles, m.p. 147°. The B.P. 1914 only recognises the nitrate, m.p. about 176°, and soluble in 8 parts of water. The U.S.P. 1916 includes both the nitrate and hydrochloride with the following constants: Nitrate, m.p. 170°–173°, soluble in 4 parts of water and in 75 parts of alcohol at 25°, and the hydrochloride, m.p. 195°–198°, soluble in 0·3 part of water and in 3 parts of alcohol at 25°. The U.S.P. evidently refers to an impure pilocarpine nitrate, as the pure salt as prepared by Jowett (*l.c.*) melts at 178° and is soluble in 6·4 parts of water at 20°.

***Iso*Pilocarpine** $C_{11}H_{16}O_2N_2$. When pilocarpine is heated alone or with alcoholic soda it is changed into *iso*pilocarpine, which also occurs in *P. microphyllus* and *P. Jaborandi* leaves, and, according to Jowett (Chem. Soc. Trans. 1900, 77, 473), is frequently found in commercial pilocarpine nitrate. It is an oil, b.p. 261°/10 mm. $[\alpha]_D = +42{\cdot}8°$ in alcohol. The nitrate $B{\cdot}HNO_3$, m.p. 159°, crystallises in prisms, and is less soluble in alcohol than pilocarpine nitrate (Jowett, *l.c.*); the hydrochloride B·HCl, m.p. 127°, is stable in the air (unlike the pilocarpine salt, which is hygroscopic). The aurichloride, m.p. 158°–159°, forms lemon-yellow needles, and the picrate, long yellow needles, m.p. 161°.

Reactions and constitution.—On solution in alkalis both alkaloids form unstable sodium salts, viz. sodium pilocarpate and sodium *iso*pilocarpate, from which salts of other metals may be prepared. On oxidation with permanganate *iso*pilocarpine produces homopilopic acid $C_8H_{12}O_4$, and pilopic acid $C_7H_{10}O_4$. The former on fusion with potash yields α-ethyltricarballylic acid, and the second, on similar treatment, gives *n*-butyric acid. By distillation with soda-lime *iso*pilocarpine yields 1 : 4- (or 5-) dimethylglyoxaline (Jowett, Chem. Soc. Trans. 1900, 77, 474, 851; 1901, 79, 581, 1331; 1903, 83, 440; *cf.* Pinner and collaborators, Ber. 1900, 33, 1424, 2357; 1901, 34, 727; 1902, 35, 2241). One of the two following formulæ is regarded as representing *iso*-pilocarpine :—

I.

or II.



*Iso*Pilocarpine (Jowett).

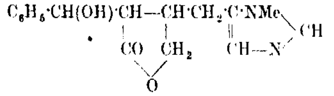
the balance of evidence being in favour of I. (Jowett, Chem. Soc. Trans. 1903, 83, 438; 1905, 87, 794; and Pyman, *ibid.* 1910, 97, 1814; *cf.* Pinner and Schwarz, Ber. 1902, 35, 2441). Pilocarpine or *iso*pilocarpine nitrate is converted by the action of alcoholic potash into an equilibrium mixture consisting chiefly of *iso*pilocarpine with a small percentage of pilocarpine and the alkaloids are thus probably stereoisomerides (Jowett, *l.c.*).

Pilocarpidine $C_{10}H_{14}O_2N_2$ occurs in *Pilocarpus Jaborandi* leaves, but not in those of *P. microphyllus*, and consequently is not obtainable from the Jaborandi leaves of present-day commerce. The alkaloid is liquid, but yields crystalline salts; the hydrochloride has $[\alpha]_D +72°$. The nitrate, m.p. 137°, $[\alpha]_D +73{\cdot}2°$ is much more soluble in alcohol than pilocarpine and *iso*pilocarpine nitrates; the aurichloride, m.p. 124°–125°, is soluble in water. As in the case of pilocarpine the optical rotation of pilocarpidine is reduced by the addition of alkali (Harnack and Meyer, Chem. Zeit. 1885, 628; Merck, Arch. Pharm. 1898, 236, 141; Jowett, Chem. Soc. Trans. 1900, 77, 474). The name pilocarpidine was erroneously applied by Petit and Polonowsky to *iso*pilocarpine.

Jaborine. This amorphous alkaloid may occur in *P. Jaborandi* leaves (Harnack and Meyer, Annalen, 1880, 204, 67). According to Jowett (*l.c.*), commercial jaborine is a mixture of *iso*pilocarpine, pilocarpidine, and possibly pilocarpine, with colouring matter.

Pilosine $C_{16}H_{18}O_3N_2$. This alkaloid was obtained from the mother liquors from which pilocarpine and *iso*pilocarpine had been isolated by Pyman (Chem. Soc. Trans. 1912, 101, 2260), and almost simultaneously by Léger-Roques, who named it 'carpiline'; it occurs to the extent of about 0·007 p.c. in the leaves of *P. microphyllus*. Pilosine forms large colourless plates, m.p. 187°, $[\alpha]_D$ +39·9° in alcohol. The rotation is reduced by alkali, as in the case of pilocarpine and *iso*pilocarpine. The salts do not crystallise well; the aurichloride B·HAuCl$_4$, golden wedge-shaped plates, m.p. 143°–144°.

Constitution.—Heated with alkali it yields benzaldehyde and pilosinine $C_8H_{12}O_2N_2$. The latter behaves like pilocarpine and *iso*pilocarpine, and the constitutional formula of pilosine is therefore probably :—



(*cf.* formula for *iso*pilocarpine I.). Both pilosine and pilosinine have a mild pilocarpine action, very much weaker than the latter base.

The microchemical detection of the alkaloids in the leaves of *Pilocarpus pennatifolius* (Lem.) has been investigated by Tunmann (Chem. Zentr. 1909, i. 1510).

Of the constituents of Jaborandi which have been examined there only remains to be mentioned the volatile oil, which exists to the extent of about ½ p.c. in the leaves. This consists of a dextrorotatory terpene which boils at 178°, pilocarpene $C_{10}H_{16}$, and some higher boiling liquid and solid compounds. Pilocarpene has the sp.gr. 0·852 and forms a crystalline hydrochloride $C_{10}H_{16}$,2HCl which melts at 49·5°.

An examination of a species of Jaborandi, *Pilocarpus spicatus* (St. Hiliare) [Aracati jaborandi (Holmes)], by Petit and Polonowsky (J. Pharm. Chim. [vi.] 5, 369) has led to the isolation of two alkaloids. The leaves were extracted in the usual way and the mixture of the bases converted into nitrates. The mixed nitrates were then treated with sodium hydroxide and extracted with chloroform. From the chloroform solution, ψ-jaborine was obtained as a colourless oil with strongly alkaline properties, yielding a crystalline nitrate, m.p. 158°. The second alkaloid ψ-pilocarpine has very much the same properties as pilocarpine, except that it is optically inactive, and yields a crystalline nitrate, small needles, m.p. 142°, and a hydrochloride, prisms, m.p. 198°. H. A. D. J.

JABORINE *v.* JABORANDI.

J-ACID. 2-*Amino*-5-*Naphthol*-7-*Sulphonic Acid* (*q.v.*).

JADE. Under this term are included two distinct minerals differing widely in chemical composition, but strikingly similar to one another in external characters. These are nephrite and jadeite. They rank as precious stones, being especially valued in the East as the material for elaborately carved ornaments. Stone implements worked in these materials have been found in the ancient Swiss lake-dwellings and amongst prehistoric remains in many other countries. These minerals have, in common, a white to green (rarely a pale violet) colour, with a certain degree of translucency and a greasy appearance on highly polished surfaces. They are remarkable for their extreme toughness (as distinct from hardness), it being very difficult to fracture pebbles by blows from a hammer. This toughness is a result of the peculiar texture of the material; thin sections examined under the microscope show a close, felted aggregate of short, minute fibres.

The name nephrite from the older name *lapis nephriticus*, meaning kidney-stone, refers to the ancient belief that when worn as a charm this stone was a remedy for kidney disease. The name jade has the same meaning, through the Spanish 'piedra de yjada.' A well-known Chinese name is 'yu,' and the ancient Mexican is 'chalchihuitl.' Jadeite was first distinguished chemically and so named by A. Damour in 1863.

Nephrite is a metasilicate of magnesium and calcium $CaMg_3(SiO_3)_4$, with usually a small and variable amount of ferrous oxide (to which is due the range in colour). It is a member of the amphibole group, differing from tremolite, actinolite, and amphibole-asbestos only by reason of the peculiar texture of the material. Under the microscope, the fibres show prismatic cleavages inclined at 124° and the optical characters of amphibole; sp.gr. 2·9–3·1; H. 6–6½.

Jadeite is a metasilicate of sodium and aluminium $NaAl(SiO_3)_2$; small amounts of ferrous and ferric oxides are often present, and in the dark green variety known as chloromelanite there is 6–10 p.c. Fe_2O_3 isomorphously replacing alumina. Jadeite is a member of the pyroxene group, having an angle of 93° between the prismatic cleavages and the optical properties characteristic of this group; sp.gr. 3·30–3·35 (3·4 in chloromelanite). The hardness (H. 6½–7) is rather greater in jadeite than in nephrite.

These two minerals are of course readily distinguished by chemical tests; and also by the easier fusibility of jadeite, which at the same time imparts a yellow colour to the flame. In thin sections under the microscope, the optical characters and cleavage angles afford distinguishing features. In many cases, however, it is the material of a carved ornament that requires determination, and then the only available test is that given by the difference in sp.gr. Some other minerals, *e.g.* the hard compact variety of serpentine known as bowenite (sp.gr. 2·6), which are often confused with jade, may also be readily distinguished by their sp.gr.

Nephrite and jadeite each occur as constituents of metamorphic silicate rocks, and they are frequently so intimately intermixed with other minerals that the material itself is at times of the nature of a rock. Much of the material used for carving is collected as pebbles and boulders from the beds of streams. Quarries in the solid rock are, however, worked in Eastern Turkestan (nephrite) and at Tawmaw in Upper Burma (jadeite). The well-known New Zealand 'greenstone' is a dark green nephrite. (On New Zealand nephrite, *see* A. M. Finlayson, Quart. J. Geol. Soc. 1909, 65, 366.)

Jade presents many points of interest to the ethnologist and collector as well as to the mineralogist, and it is the subject of a considerable literature. A monumental work in two huge, beautifully illustrated volumes is the 'Investigations and Studies in Jade,' based on the Heber R. Bishop collection (New York, 1906; a privately printed edition limited to 100 copies was prepared at enormous expense for free distribution to the principal royal and public libraries of the world). The subject is here dealt with by numerous contributors from all possible points of view; in the chemical portion 58 new analyses are given. A briefer and more accessible general account of jade is given in M. Bauer's Edelsteinkunde, 2nd edit. 1909; English translation, Precious Stones, by L. J. Spencer. 1904. L. J. S.

JADEITE *v.* Jade.

JAK-WOOD, or Jack-wood, is derived from the *Artocarpus integrifolia* (Linn.) which belongs to the *Urticaceæ*, and is cultivated throughout India, Burmah, and Ceylon, except in the north. It is largely used for carpentry, furniture, &c., and is stated to be imported to Europe for this purpose. The rasped wood is used by the natives of India and Java as a yellow dye in conjunction with alum, for the robes of the Burmese priests, also for dyeing silk and for general purposes.

An aqueous solution of the wood possesses the characteristic property that when it is treated with alkali and gently warmed, the yellow solution at first obtained assumes a beautiful blue tint.

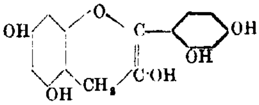
Jack-wood (Perkin and Cope, Chem. Soc. Trans. 1895, 67, 937) is very similar to old fustic, and its dyeing properties are due to *morin* (*see* Old Fustic). Unlike old fustic, however, it contains no maclurin, but there is present a second substance, *cyanomaclurin*, which is devoid of tinctorial property. These compounds can be isolated from jack-wood by methods which are almost identical with those which have been applied to fustic itself, and their separation may be effected by means of lead acetate, as this precipitates only the morin.

Cyanomaclurin $C_{15}H_{12}O_6$, crystallises in colourless prisms, somewhat readily soluble in water, and gives with basic lead acetate a colourless precipitate, and with ferric chloride a violet-coloured liquid. Its solution in dilute alkalis is colourless, but if this be gently warmed a beautiful deep indigo coloration is produced, which on longer digestion passes into green and finally beomes brown-yellow. When fused with alkali, it gives *β-resorcylic acid* and *phloroglucinol*.

Acetylcyanomaclurin $C_{15}H_7O_6(C_2H_3O)_5$, colourless needles, melts at 136°–138°, and *benzoylcyanomaclurin* $C_{15}H_7O_6(C_7H_5O)_5$, colourless prisms, melts at 171°–172°. *Disazobenzene cyanomaclurin* $C_{15}H_{10}O_6(C_6H_5N_2)_2$, scarlet needles, m.p. 245°–247° (decomp.), gives an *acetyl* derivative, probably

$$C_{15}H_7O_6(C_6H_5N_2)_2(C_2H_3O)_3$$

orange-red needles, m.p. 209°–210° (decomp.) (Perkin, Chem. Soc. Trans. 1905, 87, 715). In certain respects, cyanomaclurin resembles the catechins of gambier and acacia catechus, and more especially so in that by boiling with dilute acids it gives reddish-brown amorphous substances, which are very similar to the so-called catechin anhydrides. The product obtained by the action of hydrochloric acid on a boiling acetic acid solution of cyanomaclurin is insoluble in alkalis and all solvents, and has a percentage composition almost identical with the catechin anhydride similarly produced. According to Perkin, cyanomaclurin is possibly a reduction product of morin, thus:



Jack-wood dyes shades very similar to those given by old fustic; that is, olive-yellow with chromium, dull yellow with aluminium, and a brighter yellow with tin mordant. On the other hand, the sample examined by Perkin and Cope possessed only about one-third of the dyeing power of old fustic. A. G. P.

JALAP *v.* Resins.

JALAPIN *v. Scammony*, art. Gum resins; Glucosides.

JAMBA OIL is obtained from a plant belonging to a variety of the genus *Brassica*. The oil behaves, in most respects, very similarly to ordinary rape oil, but differs from it most distinctly in that it does not lend itself so readily to the manufacture of 'blown' oil as the other oils belonging to the rape oil group. Hence jamba oil is distinctly inferior to rape oil prepared from genuine rape seed oil, which accounts for its lower commercial value as compared with that of colza oil.

Jamba oil is most readily recognised by its peculiar taste and smell. It is chiefly used as a burning oil, although it does not burn so well as colza oil. It is also used for lubricating purposes, and takes its place, as regards quality, between Indian rape oil and ravison oil.

The following values have been recorded for genuine specimens of the oil: sp.gr. 0·9150–0·9158; solidification point, −10° to −12°; iodine value, 95·2–102·5; and m.p. of fatty acids, 19°–21°.

JAMESONITE. A sulphantimonite of lead, invariably containing 2–3 p.c. of iron, the formula being $4PbS{\cdot}FeS{\cdot}3Sb_2S_3$ (W. T. Schaller, Zeitsch. Kryst. Min. 1911, 48, 562; L. J. Spencer, Min. Mag. 1907, 14, 207, 310). It is orthorhombic with a distinct basal cleavage, but only acicular crystals (*v.* Feather-ore), columnar masses, or more usually finely fibrous masses have been found. Coarse columnar masses associated with stibnite have been mined at Endellion in Cornwall. The mineral is of frequent occurrence in Bolivia, and, as it sometimes contains small amounts of silver, it has been worked as a silver-lead ore as well as for antimony. L. J. S.

JANTHONE. A synthetic perfume obtained by condensing critral or lippial and mesityl oxide. *Lippial* $C_{10}H_{16}O$ is present in the oil of *Lippia citriodora* (H. B. & K.). Janthone is a tetrahydrobenzene derivative containing two ethylene bonds in the ketone side chain: b.p. 162° under 10 mm.; sp.gr. 0·9452. When diluted it has a characteristic odour of violets and orris root. (D. R. P. 118288, 1898; Farbw. Durand, Hugenin & Co., Zeitsch. angew. Chem. 1901, 14, 346.)

JAPAN BLACK *v.* Brunswick black.

JAPAN EARTH. *Terra japonica v.* Catechu.

JAPANESE SARDINE OIL is obtained from *Clupanodon melanosticta* (T. and S.), a fish belonging to the *Clupeidæ*. Japanese sardine oil differs distinctly from the ordinary sardine oil (*see* SARDINE OIL) in its higher iodine value, which in pure specimens reaches as high a figure as 187. The commercial oil has, until recently, been prepared in a very crude manner, the fish refuse having been boiled with water to separate the oil. Japanese sardine oil is characterised by a considerable proportion of *clupanodonic acid*, of which as much as 14·2 p.c. is yielded by genuine specimens.

Genuine specimens examined by Tsujimoto gave the following values: Sp.gr. at 15·5°, 0·9316–0·9347; saponification value, 194·8–196·2; refractive index at 20°, 1·4802–1·4808; iodine value, 180·6–187·3; and m.p. of fatty acids, 35·4°–36·2°.

The commercial Japanese sardine oil has hitherto been more or less mixed with other fish oils, so that the commercial specimens of oil have much lower iodine values than the genuine oils. Japanese fish oil (which must not be confounded with Japanese cod-liver oil) is largely exported to Europe and to Australia, where it is used in soap making and in the leather industries. J. L.

JAPAN WAX (Japan tallow) is obtained from the berries of several species of the sumach tree, viz.: *Rhus succedanea* (L.), known in Japan as 'hazé'; *R. acuminata* (DC.); *R. vernicifera* (DC.), known in Japan as 'urushi-noki'; *R. sylvestris* (Sieb. et Zucc.). The first-named species is grown chiefly in China, whereas the last-named one flourishes especially in the western provinces of Japan; the species *R. succedanea* grows also in Indo-China and in India. In China, Japan, and Tonkin, the trees are cultivated chiefly for the sake of the lacquer which they exude. Japan wax must therefore be considered as a by-product of the lacquer industry.

The seeds of the several species of *Rhus* consist of a small kernel surrounded by a greenish, striated, shrivelled mass. In China the wax is prepared by crushing the seeds, together with their coating, and steaming them in perforated cylinders so that the fat melts and runs off. In Japan the manufacture is still carried out in a somewhat crude fashion, by storing the berries in straw until they are fully matured, then crushing them by hand in a wooden funnel-shaped trough, and winnowing the mass so as to separate the kernels. The powdered mass thus obtained is put into hempen sacks and subjected to pressure in wooden wedge presses. The yield from the berries ranges from 15 to 20 p.c. The fat is a coarse greenish tallow-like mass. It is refined by remelting, pressing through cotton sacks, and allowing the fat to drop into cold water. The thin flakes of the wax are then bleached by exposure to the sun in shallow baskets (in a similar manner as is done in the process of bleaching beeswax), the material being continually turned over and sprinkled with water. The bleached wax is finally melted and cast into slabs, in which form it is exported to Europe.

The production of Japan wax cannot be largely extended, as it takes 7 to 8 years for a wax tree to reach maturity, and if the tree promises to become a fruitful source of lacquer, this leads to its sacrifice as a source of wax.

Japan wax is a pale yellow, slightly hard substance of conchoidal, somewhat lustrous fracture. On keeping, Japan wax turns deep yellow and becomes coated with a white powder consisting of microscopical prismatic needles. The term 'wax' is a misnomer, as Japan wax is a glyceride, consisting chiefly of palmitin and free palmitic acid. Hence, it is more appropriately termed Japan tallow.

Japan wax is insoluble in cold alcohol, but dissolves readily in boiling alcohol, separating almost completely on cooling as a granular, crystalline mass. In addition to palmitic acid, which differs in some respects from the palmitic acid from animal fats, it also contains small quantities of dibasic acids, as also of a soluble acid, the proportion of which has been found to amount to almost 6 p.c. The proportion of dibasic acids amounts to nearly 1 p.c.; amongst these, the largest in amount is *japanic acid* $C_{19}H_{38}(COOH)_2$ (nonadecamethylenedicarboxylic acid), which is accompanied by its lower homologues, heptadecamethylenedicarboxylic acid $C_{17}H_{34}(COOH)_2$, and octodecamethylenedicarboxylic acid $C_{18}H_{36}(COOH)_2$. These dibasic acids probably occur as mixed glycerides of palmitic and dibasic acids. The constitution of Japan wax being that of a glyceride, it is most readily differentiated from the true waxes by yielding glycerol on saponification. The iodine value of genuine Japan wax is about 4. The commercial wax has a higher iodine value—from 10 to 15—as in consequence of the increased demand for Japan wax it has become the practice in Japan to extract the press residues with the (hazé) kernel oil. In the Chinese mode of manufacture, the kernel oil passes automatically into the 'wax.' At a temperature of 16°–18°, Japan wax has the density of water of the same temperature.

The wax melts at about 50°–60°, and it shows the phenomenon of double melting-point, a sample melting many degrees lower after having once been melted and rapidly cooled. It has sp.gr. of 0·984–0·993 at 15°, Hehner value, 189–191, and its insoluble fatty acids melt at about 54°–62°. The commercial product usually contains about 0·06 p.c. of mineral matter.

Japan wax is largely used for waxing floors, and as a constituent of polishes. As it forms an emulsion with water, it can be used for currying leather. Notwithstanding its high proportion of palmitic acid, it does not constitute a suitable candle material. The proposal to use it as an admixture with edible fats, or with margarine, is to be strongly deprecated. The adulterants of Japan wax include water and starch, whilst, on the other hand, it has been used as an adulterant of beeswax. J. L.

JAPACONITINE *v.* ACONITINE.

JAPANESE WAX *v.* *Insect wax*, art. WAXES

JAPANIC ACID *v.* JAPAN WAX; AND WAXES.

JAPANNING. A term synonymous with 'lacquering' (*v.* LACQUER).

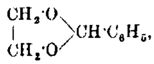
In Europe, japanning is also taken to mean the art of coating surfaces with varnishes which are then hardened by subjecting them to a high temperature, an art which holds an intermediate position between painting and enamelling. The varnishes are transparent and durable bodies, in black or other colours, black being the hue which is most extensively used. Black varnish is composed of pure natural asphaltum mixed into a preparation of gum anime dissolved in linseed oil and turpentine. This in thin coatings appears brown, and requires several courses to acquire the requisite blackness; the article treated being placed in a stove at about 150° after each coating. For colours, the necessary mineral pigments or metallic powders are mixed with a transparent copal varnish of less body than ordinary painters' varnish.

European japanning, although very far behind the work produced by the process described as in use among the Japanese, produces a very brilliant and durable coating to small articles of metal work and papier mâché. It is also applied as a facing for stone to imitate marble.

JAPAN SAGO. Starch obtained from the stem of *Cycas revoluta* (Thunb.).

JARGON or **JARGOON** *v.* Zircon.

JAROSITE. Hydrated basic sulphate of potassium and ferric iron $K_2O{\cdot}3Fe_2O_3{\cdot}4SO_3,6H_2O$ or $K_2Fe_6(OH)_{12}(SO_4)_4$, crystallised in the rhombohedral system and isomorphous with alunite. The potassium (K_2O, 9·4 p.c. according to the formula) is often partly replaced isomorphously by sodium, Na_2O reaching 6·18 p.c. in the variety *natrojarosite*; and in the variety *plumbojarosite* lead (PbO, 19·7 p.c.) takes the place of potassium. The small crystals have the form of cuboidal rhombohedra, the interfacial angles being 90° 45′; or they may be tabular in habit owing to the predominance of the basal planes. Closely aggregated they line cavities in the massive material, or they may be loose as a glistening powder. The mineral also forms granular, fibrous, and concretionary masses. The colour is yellowish-brown and the streak ochre-yellow; sp.gr. 3·1–3·2 (3·66 in plumbojarosite); H. 2½–3½. The name is from the Jaroso ravine in the Sierra Almagrera, Spain, where the mineral occurs with limonite in a silver-lead mine. Several other localities are known, especially in Bohemia and the United States. L. J. S.

JASMAL. The active odoriferous principle of the jasmine flower. Is the methylene acetal of phenyl glycol,  $\begin{matrix}CH_2{\cdot}O\\ |\\ CH_2{\cdot}O\end{matrix}{>}CH{\cdot}C_6H_5$, and may be synthetically formed by condensation of phenyl glycol and formaldehyde in presence of sulphuric acid; b.p. 218°; sp gr. 1·1334 (Verley, Compt. rend. 1899, 128, 314).

JASPER. A compact and opaque variety of quartz, intimately intermixed with iron oxide and hydroxide, clay, &c.; these impurities being present sometimes to the extent of 20 p.c. The material has a dull, even fracture, but it takes a good polish; the colours are various—red, yellow, brown, green, &c. It is cut and polished as an ornamental stone, and was much prized by the ancients, but their *jaspis* included other minerals than those now designated as jasper. The well-known *Egyptian jasper* is found as nodules and pebbles in the Nile Valley, and resembles a brown flint, with dark zones and cloudings. *Banded jasper* is a striped variety, well illustrated by the beautiful red and green 'riband jaspers' of the Ural Mountains. Some banded jaspers appear to be metamorphic sedimentary rocks, whilst others are striated felsitic tuffs. The so-called *porcelain-jasper* is merely a shale highly indurated by exposure to a high temperature.

Agate-jasper or *jasp-agate* is intermediate in character between jasper and agate or chalcedony; and in other directions no sharp line can be drawn between jasper and hornstone or chert, all of which are simply compact varieties of quartz.

Red jaspers owe their colour to intermixed ferric oxide. They are sometimes so highly ferruginous and interlaminated with bands of hæmatite that they constitute ores of iron, *e.g.* the so-called *jaspilite* of the Lake Superior district. L. J. S.

JASPILITE *v.* Jasper.

JATEORRHIZINE *v.* Calumba.

JAUNE ACIDE. *Acid yellow* (*v.* Azo-colouring matters).

JAUNE ANGLAIS. *Victoria yellow* (*v.* Cresol).

JAUNE BRILLIANT. *Cadmium sulphide* (*v.* Cadmium).

JAUNE DE FER, JAUNE DE MARS. *Mars yellow* (*v.* Pigments).

JAUNE D'OR. *Martius's yellow* (*v.* Naphthalene).

JAUNE N. *Curcumein*; *Orange N.* (*v.* Azo-colouring matters).

JAUNE SOLIDE. *Fast yellow* (*v.* Azo-colouring matters).

JAVA WAX, FIG WAX *v.* Waxes.

JECORIC ACID $C_{18}H_{30}O_{21}$. An isomer of linolenic acid, said to occur in sardine oil and other fish oils, associated with clupanodonic and aseltinic acids.

JERVINE *v.* Cevadine.

JESACONITINE *v.* Aconitine.

JESSENIA POLYCARPA (Karst.). The nuts of this Colombian palm, known locally as the 'sejen' or 'unamo' palm, yield a pale yellow oil closely resembling olive oil in physical and analytical characters. It is used in Bogota and other Colombian towns for culinary and medicinal purposes and could, presumably, be used for all purposes for which olive oil is employed (Bacharach, Analyst, 1918, 289).

JESTERIN *v.* Glucosides.

JET. (Fr. *Jais, Jaiet*; Ger. *Gagat, Agstein.*) A variety of fossil coal or lignite, similar in appearance to cannel-coal. Being hard (H. 3–4) and capable of taking a lustrous surface by polishing, it is used for making small ornamental articles; sp.gr. 1·35. It is found on the Yorkshire coast near Whitby, in Spain, France, and Wurtemberg, occurring in the shale and limestone formations. The name is supposed to be a corruption of the *Gagates* of Pliny and Dioscorides, who described the mineral as found near the mouth of the river Gagas in Lycia, Asia Minor.

The jet of Whitby is evidently a fossilised coniferous wood, as shown by its structure in thin sections under the microscope. On its surface impressions of fossils, especially ammonites, frequently appear.

Whitby jet is divided into 'hard' and 'soft,' of which the former is the more esteemed; it is found near the base of the Upper Lias and, sparingly, in other parts of that formation. Soft jet occurs in the sandstones and oolitic shales. The hard variety is obtained in compressed layers varying from an inch or two in length and ⅛th in thickness, to 6 feet long, 30 inches wide, and 4 inches thick. The largest piece ever found was 6 feet 4 inches long, 4½ to 5½ inches wide, and 1 and 1½ inches thick; it weighed 11 lb. 8 oz.

The collection of jet was formerly effected by cutting down the cliffs until the jet-veins showed themselves; to-day the cliffs are almost abandoned and the works are carried on inland to a distance of 20 miles. The operation is described by J. A. Bower (Jour. Soc. of Arts, 22) in these words: 'The process of obtaining jet here is simple; the faces of the hills are turned down bodily, and by then tunnelling for some distance, and after carrying several passages parallel from the face of the hill, transverse shafts are cut. When the rock becomes too hard the miners retire, pulling down the roofs on their return; in these falls the bulk of the jet is found.' The rough jet obtained from the inland mines is encased in a brown skin; that from the cliffs is covered with a blue skin. This is chipped off, the pieces of jet are sawn into suitable sizes and handed over to the carver or turner. (*See* J. A. Bower, Whitby Jet and its Manufacture, Jour. Soc. of Arts, 1874, 22, 80; John Phillips, Illustrations of the Geology of Yorkshire, Part I. The Yorkshire Coast, 1835; 2nd ed. 1875; A. C. Seward, The Structure and Origin of Jet, Rep. Brit. Assoc. 1901, 856; P. E. Spielmann, The Origin of Jet, Chem. News, 1906, 94, 281; 1908, 97, 181. Special Reports on the Mineral Resources of Great Britain, Mem. Geol. Survey, 1918, vol. 7.) L. J. S.

JOHANNITE. Hydrated sulphate of uranium (UO_3, 67·7 p.c.) and copper of uncertain formula. Sp.gr. 3·19; soluble in water. It occurs as small, transparent, green, monoclinic crystals as an alteration product of pitchblende at Joachimsthal in Bohemia and Johanngeorgenstat in Saxony. L. J. S.

JOSEITE *v.* TETRADYMITE.

JUAR-ROOT. A powerful narcotic used in India to enhance the intoxicating power of bhang.

JUDSON POWDER *v.* EXPLOSIVES.

JUGLONE *v.* NAPHTHALENE.

JUNIPER. (*Genièvre*, Fr.; *Wacholder*, Ger.) The berries have been employed in medicine from very early times and have sometimes been used as an article of food. They are a reputed diuretic. The large proportion of dextrose (15–20 p.c.) renders them available for fermentation and the distillation of spirit. Such a product was in France called *genièvre*, and hence the contracted form *gin* employed in this country for a spirit which now is merely flavoured with juniper.

The *essential oil* from the berries, *Oleum juniperi* (B.P.; U.S.P.) is now alone official, and is obtained from the ripe fruits of *Juniperus communis* (Linn.) (Bentl. a. Trim. 255), a well-known evergreen shrub which inhabits the northern regions of both hemispheres. The fruits are gathered chiefly in Hungary, Austria, and Southern France (Flück. a. Hanb. 624; Morel, Pharm. J. [iii.] 8, 886). The oil is a colourless or pale yellow-green limpid liquid of aromatic burning taste. The density is generally between 0·867 and 0·875 (0·862–0·890 at 15·5°, B.P.; 0·854–0·879 at 25°, U.S.P.); $[a]_D$ −3° to −15°; usually −4° to −6°; $n_{25°}$ 1·472–1·488. On keeping the oil gradually resinifies and becomes viscid, and the density increases. The chief constituents are *pinene*, b.p. 156°, predominating in the oil from unripe fruits (65 p.c. or more), a sesquiterpene *cadinene*, b.p. 274°; and *terpene alcohols*, particularly *terpineol*, b.p. 209°–212°; the higher boiling constituents predominate in the oil from ripe fruits, which also contains small quantities of *juniper camphor*, m.p. 165°–166°, and an *ester*, perhaps terpineol acetate. According to the B.P. the oil should dissolve in 4 parts of 95 p.c. alcohol. An alcoholic solution is largely used as *gin essence*. The oil from the leaves is very similar but dextrorotatory, $[a]_D = +8° 46'$.

Oil of cade (*Oleum cadinum*, B.P.; U.S.P.) is a reddish-brown or nearly black liquid obtained by destructive distillation of the woody portions of *Juniperus Oxycedrus* (Linn.). It has a specific gravity of about 0·980–1·055 at 25° (U.S.P.). The principal constituent is cadinene, and the oil is incorporated in ointments and soaps for use in skin diseases. G. B.

JUNIPER, OIL OF, *v.* OILS, ESSENTIAL.

JUTE is the bast fibre almost exclusively of two plants of the natural order *Tiliaceæ*, viz. *Corchorus capsularis* (Linn.) and *Corchorus olitorius* (Linn.), cultivated for the most part in Bengal, where they are indigenous. Although differing in size and in the form of their seed-pods, the plants are not greatly dissimilar in appearance and are not commercially distinguished from each other. The seed is sown annually, in April or May, and the plants after flowering, which takes place from August to September, and having now attained a height of 5 or 6 feet in the case of *C. olitorius*, and of 5 to 10 feet in that of *C. capsularis*, are cut down and thrown into pits of water to soak, after the manner of steeping flax. From a few days to a month is required to bring the stalks into a condition for stripping the bast from the wood and freeing it from cortex, these operations being purely manual. After being washed and dried the jute is made up into bales for sale.

Jute is very largely used for the manufacture of sacking and wrapping cloths (Hessians), as a paper-making fibre, and as a substitute for hair in making theatrical wigs. It is also employed for carpet-making and inferior cordage and, in India, for making small domestic articles such as nets and muzzles for oxen. In these islands the principal seat of the jute industry is Dundee.

The fibre occurs in strands of considerable length, 6–12 feet; the spinning unit or filament is of various lengths, according to the degree of subdivision practised. The filament is a complex of the ultimate fibres, of which from 5 to 12 are usually seen in the section at any point. They are polygonal in section and much thickened (lignified); their length does not exceed 2–3 mm., whereas those of flax and hemp—also bast fibres—are from 25–40 mm. long. This structural inferiority, together with the fact that the fibre substance yields somewhat readily to the action of oxidants (air and light) in presence of water, characterises jute as a 'weak fibre.'

Treated by the 'line spinning' process it may be spun into yarns of considerable fineness, but, owing to the large proportion of waste ('tow'), at relatively large cost. These yarns when bleached—preferably by 'soda bleach' (sodium hypochlorite)—have considerable lustre; they are soft and of a cream shade, and take up the majority of colouring matters—wood and aniline dyes—directly from the dye-bath. Jute fabrics are also successfully printed in steam styles, the presence of sodium sulphide being necessary to preserve the fibre substance from the action of the steaming process (Développement de l'Industrie de Jute, Cross and Witt, Bull. Mulhouse, 1881).

According to the investigations of Cross and Bevan, jute does not contain cellulose as such, but in the form of bastose or lignocellulose, which is a link between the carbohydrates and the aromatic compounds. Treated with chlorine it gives a yellow chlorinated derivative which when hydrolysed yields substances belonging to the tannic acid group. Hence it may be said that jute possesses a mordant which makes it receptive of aniline colours in a degree possessed by none of those fibrous materials which require the intervention of a mordant. When quantities of the fibre are kept in a damp situation, more especially when exposed to sea-water, it is decomposed into substances analogous to tannin and to acids of the pectic acid group. Under treatment by acids, jute is disintegrated, yielding xylose and furfural (v. also Tollens, Annalen, 254, 325). It is easily bleached by potassium permanganate after cleansing with soap or alkali, with a loss in weight of 3 to 4 p.c. In practice this is generally too expensive a process, and the substances usually employed are hypochlorites, in which great care is necessary, as chlorinated compounds may be formed and the fibre destroyed (*supra*) (v. Cellulose).

K

K ACID. 1-*Amino*-8-*Naphthol*-4:6-*Disulphonic acid*

KACHIN. A pyrocatechol photographic developer.

KAFIRIN. The alcohol-soluble protein of kafir; closely resembles zein, the alcohol-soluble protein of maize, but differs from it in containing a small quantity of tryptophan, in addition to leucine and glutamic acid, but is free from glycine (Jones and Johns, J. Biol. Chem. 1918, 36, 323).

KAINITE. A hydrated double salt

$$MgSO_4 \cdot KCl,3H_2O,$$

occasionally found in the potash-salt deposits as sharply-developed, water-clear, monoclinic crystals; sp.gr. 2·13, H. 2½–3. It contains KCl 30 p.c. (K 18·9 p.c.). As granular masses of a white, grey, or reddish colour, it forms large beds near Stassfurt in Prussia, Asse in Brunswick, and at Kalusz in Poland (v. Potassium). It occurs, intermixed with kieserite, carnallite, rock-salt, and anhydrite, in the uppermost layers of the 'carnallite zone.' The mineral was first recognised in 1865 in the Anhalt shaft at Stassfurt, and was named from καινός, new, with the mineralogical termination *ite*. Unfortunately, the German spelling 'Kainit' is in common usage, although the correct English equivalent is familiar to mineralogists. Raw kainite is extensively used as a fertiliser, and it is also employed for the preparation of potassium chloride and sulphate. On the artificial production of kainite, *see* van 't Hoff, Sitz.-Ber. Akad. Wiss. Berlin, 1901, 420; 1903, 678.

L. J. S.

KAIRINE, KAIROCOLL, KAIROLINE, v. Quinoline.

KAISERGELB v. Aurantia.

KAISERROTH. The sodium salt of dinitrodibromfluorescein. Called also Eosin Scarlet, Safrosine, and Lutétienne.

KALADANA, (B.P.), or **PHARBITIS SEEDS.** The dried seeds of *Ipomœa hederacea* (Jacq.).

KÄLIASTRAKANITE KALIBLODITE, v. Leonite.

KALIBORITE. Hydrate borate of magnesium and potassium $K_2Mg_4B_{22}O_{38},14H_2O$ crystallised in the monoclinic system. It occurs as small, colourless to white, crystals embedded in nodules of sulphur-yellow pinnoite ($MgB_2O_4,3H_2O$) in the 'carnallite zone' and the overlying potash-salts at Leopoldshall near Stassfurt and Westeregeln in Prussia. Sp.gr. 2·12, H. 4-5; readily soluble in hydrochloric acid. Curiously, the mineral was twice described independently in 1890 under the names heintzite and hintzeite; whilst in the previous year a massive, granular form, from Schmidtsmannshall near Ascherleben, was described under the name kaliborite. The last name has priority besides being descriptive. On the artificial production *see* van 't Hoff, 1902. L. J. S.

KALINITE. The mineralogical name for native potash-alum $K_2SO_4 \cdot Al_2(SO_4)_3,24H_2O$. Although readily obtained artificially as sharp octahedral crystals, the natural mineral usually occurs as white silky fibres, or less often as granular masses. It is found as an efflorescence on shale, having been produced by the action of the products of decomposition of pyrites on the aluminous rock (*e.g.* at Whitby in Yorkshire); or as a volcanic sublimation (*e.g.* at Vulcano in the Lipari Islands, and Vesuvius). The alum from Vulcano contains traces of caesium and rubidium. Since the mineral has been formed at the surface and is readily soluble in water, it is never found in large masses.

L. J. S.

KALIOPHILITE v. Nephelite.

KALMOPYRIN or **SOLUBLE ASPIRIN.** Trade names for calcium acetylsalicylate.

KAMALA or **KAMELA** is the orange-red powder which exists as a glandular pubescence on the exterior of the fruits of the *Mallotus phillipinensis* (Muell.) (*Rottlera tinctoria* [Roxb.]), a small evergreen tree, met with throughout tropical India, Burma, and Ceylon, also in Java, China, the Malay Islands, and Australia. The ripe capsules are gathered in February or March, and shaken in bags until the powder separates.

Kamala is employed by the Hindoos as an

antithelmic drug and for dyeing silk and wool a bright orange colour. The fabric is dyed in a boiling bath containing 4 parts kamala, 1 part alum, and 2 parts sodium carbonate (native barilla), previously well rubbed together in the powdered state with a small quantity of oil of sesamum. The alum is sometimes omitted, but the addition of alkali is absolutely necessary in order to dissolve the colouring matter, which is of a resinous character and quite insoluble in water. Kamala is also apparently used for the adulteration of annatto, for according to Perkin (private communication), samples of calico obtained from India and presumably dyed with kamala have proved on examination to owe their colour partially if not entirely to annatto. Kamala was formerly employed in this country as a remedy for *taenia*, but appears now to be very little used for this purpose.

Anderson was the first chemist to investigate kamala (Edin. New. Phil. J. 1, 300), and he isolated from it by means of ether a crystalline compound *rottlerin* $C_{11}H_{10}O_3$, a wax $C_{26}H_{34}O_4$, and a resin melting below 100°, to which he gave the formula $C_{30}H_{30}O_7$. Leube (J. 1860, 562) was unable to obtain any crystalline product from this drug, but he describes two resins, $C_{15}H_{18}O_4$, m.p. 80°, and $C_8H_{12}O_4$, m.p. 191°. Oettingen (Dissert. St. Petersburg, 1862) also could not obtain any crystalline substance from kamala. A. and W. Perkin (Ber. 1886, 19, 3109), however, isolated the crystalline rottlerin ('mallotoxin') of Anderson, and its existence was subsequently confirmed by Jawein (Ber. 20, 182).

As the result of a more extended examination of kamala and employing carbon disulphide for the extraction, A. G. Perkin (Chem. Soc. Trans. 1893, 63, 975) isolated not only Anderson's compounds, but small quantities of two crystalline substances, homorottlerin, which is yellow, and *iso*rottlerin, a salmon-coloured powder, together with a high melting resin.

Rottlerin $C_{33}H_{30}O_9$ (Perkin, *ibid.* 1895, 67, 230), salmon coloured plates, melts at 191°–191·5° (P.), 200° (Jawein), 202°–204° (Telle, Arch. Pharm. 1906, 244, 441), readily soluble in ether. Solutions of the alkali carbonates and hydroxides dissolve rottlerin, the former only on gently warming. On boiling these orange-coloured liquids, decomposition gradually takes place, an odour of benzaldehyde is evolved and a resinous product separates. An alcoholic solution of rottlerin is coloured brown on the addition of ferric chloride.

Acetylrottlerin $(C_{11}H_8O_3(C_2H_3O)_2)_3$, yellow crystalline powder, m.p. 130°–135° (P.), and *benzoylrottlerin* $C_{33}H_{24}O_9(C_7H_5O)_6$, yellow powder (Bartolotti, Gazz. chim. ital. 24, [ii.] 480), have been prepared.

Rottlerin forms the following salts:

$$C_{33}H_{29}O_9Na,H_2O$$

orange-brown glistening leaflets; $C_{33}H_{29}O_9K,H_2O$ leaflets; $(C_{33}H_{29}O_9)_2Ba$, minute reddish-brown prisms; $(C_{33}H_{29}O_9)_2Sr$, $(C_{33}H_{29}O_9)_2Ca$, and $C_{33}H_{29}O_9Ag$, fine yellow needles.

Fused with alkali, rottlerin gives *benzoic acid, acetic acid*, and *phloroglucinol* (P.); and when oxidised with hydrogen peroxide in alkaline solution, *benzaldehyde* and *benzoic acid* are produced. With potassium permanganate (Bartolotti), benzoic acid is also formed. Nitric acid (sp.gr. 1·5) gives *p-nitrocinnamic acid, o-nitrocinnamic acid, p-nitrobenzaldehyde*, and *p-nitrobenzoic acid* (P.). When heated with 2 p.c. sodium carbonate solution, a compound termed *rottlerone* separates (P.), which crystallises in garnet-red prisms, and to which the formula $C_{29}H_{26}O_6$ has been provisionally assigned.

According to Telle, if rottlerin is heated for 10 minutes with barium hydroxide solution, *phloroglucinolmethylether*, a resinous substance and *ψ rottlerin*, m.p. 235°, are produced. When heated for 10 minutes with zinc powder and sodium hydroxide, rottlerin gives 60 p.c. of resin and about 30 p.c. of phenols, also *β-phenylpropionic acid*, acetic acid, and a small quantity of a crystalline acid, m.p. 185°–185·5°. From the mixture of phenols, *phloroglucinolmonomethylether* and *phloroglucinoldimethylether*, were isolated. *Phloroglucinoltrimethylether* and a camphor-like substance, m.p. 170°–172°, were produced, when, with the zinc powder, only 2 p.c. sodium hydroxide solution was employed. The molecular weight of rottlerin, determined cryoscopically in naphthalene, was 486, and agrees with that assigned to this substance by Perkin (*l c.*).

Homorottlerin $C_{33}H_{30}O_9$ (?), pale yellow needles, m.p. 192°–193°, is present in exceedingly small amount in kamala. It differs from rottlerin in being much less soluble in toluene chloroform, or acetic acid, but otherwise the properties of these two compounds are similar (P.).

iso-Rottlerin $C_{12}H_{12}O_5$ (?), has been obtained in the form of plates, m.p. 198°–199°, insoluble in hot benzene, carbon disulphide, or chloroform. Cold solutions of the alkali carbonates dissolve it readily, and these solutions when boiled do not deposit resinous matter or emit an odour of benzaldehyde, as is the case with the alkali salts of rottlerin itself. It is probable that this compound, very little of which has been yet obtained, may prove to consist of hydroxyrottlerin (P.).

The low-melting resin of Anderson, $C_{30}H_{30}O_7$ (?) $C_{12}H_{12}O_5$(?) (P.), consists of a brittle transparent dark red mass, melting below 100°, and is readily soluble in carbon disulphide, ether, or chloroform. With hot alkaline solutions, it behaves similarly to rottlerin and evolves an odour of benzaldehyde, and with nitric acid (sp.gr. 1·5) gives *p*-nitrobenzoic acid. Perkin's *high-melting resin* is a pale straw-coloured mass, m.p. about 150°, and in general properties resembles the low-melting variety.

According to Hummel and Perkin (J. Soc. Chem. Ind. 1895, 14), for silk dyeing it is best to add 1 part of kamala, and 0·5–1 part sodium carbonate to boiling water, then to enter the silk and to dye at the boiling temperature for 2–5 minutes only. Other experiments indicated that the amount of sodium carbonate to employ should be regulated by the quantity of water used rather than by that of the kamala; namely at the rate of 13–14 grams (Na_2CO_3,10aq) per litre. After dyeing for a short time with the addition of alkali only, to the extent of one-fifth of the weight of the kamala used, the addition of alum of stannous chloride to the dyebath makes the colour fuller and more orange. A similar but by no means identical effect is obtained by making a slight addition of sulphuric acid.

As pointed out by Perkin (*l.c.*), rottlerin is decomposed by boiling sodium carbonate solution, and the colour ultimately fixed on the fibre most probably consists of rottlerone. Although rottlerin itself does not dye mordanted fabrics, the potassium and sodium salts of this colouring matter give on calico mordanted with aluminium and iron, pale orange red and brownish-black shades.

Pure Java kamala contains, according to Flückiger (Arch. Pharm. 1892), 1·363 to 1·488 p.c. of ash, whereas in the kamala examined by Anderson (*l.c.*), 3·49 p.c. was present. The best commercial varieties usually contain about 5 p.c. of mineral matter (Seidler and Waage, Ber. Deut. pharm. Ges. 1891, 80); but the inferior qualities are highly adulterated (50 to 87 p.c.) with sand, earthy impurities, red brick-dust, &c. (Perkin (*l.c.*) and J. Soc. Chem. Ind. 1900). A. G. P.

KAMALA RESINS *v.* RESINS.

KAMBARA EARTH. A product of the type of fuller's earth or Florida earth, usually of a white or yellowish colour, sometimes bluish and occasionally greenish, found in the province of Echigo, and in Fukushima and Ishi Rawa, Japan. It is said to be more efficient than fuller's earth as a decolorising agent; appears to be composed chiefly of aluminium silicate and silicic acid. The decolorising power of the earth is increased by heating to 100°-150°. Its action appears to depend upon its acidity, fineness, and proportion of hydrates of silica. It decolorises crude petroleum, and is useful for the purification of animal and vegetable oils. (Kobayashi, J. Ind. Eng. Chem. 1912, 4, 891; Ueno, *ibid.* 1915, 7, 596; J. Soc. Chem. Ind. 1913, 32, 12; *ibid.* 1915, 7, 596.)

KAMPHERITRIN *v.* GLUCOSIDES.

KAOLIN *v.* KAOLINITE.

KAOLINITE. A mineral species consisting of hydrated aluminium silicate $H_4Al_2Si_2O_9$, crystallising in the monoclinic system. Analyses of the pure crystallised material agree closely with the theoretical quantities: SiO_2, 46·5; Al_2O_3, 39·5; H_2O, 14·0 p.c. The water is expelled only at a high temperature (above 330°). As a white, glistening, crystalline powder, the mineral is occasionally met with in small amount in cavities and fissures in sedimentary rocks and in mineral veins. The best crystals have been found near Almwch in the island of Anglesey, and in the National Bell mine near Silverton in Colorado. These crystals have the form of six-sided plates or pyramids with a perfect micaceous cleavage parallel to the base; and do not exceed 0·1 to 0·2 mm. across. Their mean index of refraction is 1·563, and their birefringence (0·004) is much lower than that of mica (with small scales of which the mineral might be confused); sp.gr. 2·62; H. 2½. On the optical characters of crystals of kaolinite, *see* A. B. Dick, Min. Mag. 1888, 8, 15; 1908, 15, 124; A. Johnsen, Centr. Min. 1911, 33. The 'nacrite' of the Einigkeit mine, Freiberg, Saxony, and 'pholerite,' also from Saxony, form fan-shaped aggregates of rather larger pearly scales of kaolinite.

The mineralogical name *kaolinite* was proposed by S. W. Johnson and J. M. Blake in 1867 for this crystallised mineral, which is usually assumed to form a large part of kaolin or china-clay. The name *kaolin* is a French corruption of the Chinese name *kau-ling* for the white, earthy material long used in the manufacture of porcelain at King-te-chin (prov. Kiangsi), and first brought to Europe in the year 1712. This material is obtained in the neighbouring Kau-ling Hills (= 'high ridge') from a compact green stone occurring in clay-slates, and somewhat resembling jade in appearance, from which when crushed the finer particles are separated by washing (F. von Richthofen, Amer. J. Sci. 1871, 1, 180). This material, although a hydrated aluminium silicate, differs essentially from our kaolin, containing as much as 73 p.c. of silica and only a few p.c. of water. It is perhaps the same as the Japanese 'rōseki,' which has been referred to the agalmatolite (*q.v.*) variety of pyrophyllite.

It is thus seen that the name kaolin has been loosely applied to any white clays suitable for the manufacture of porcelain (*v.* CLAY), such as those found near Limoges in France, St. Austell in Cornwall, &c. These white clays have been formed by the decomposition of granite under somewhat special conditions; and when separated from grains of quartz, scales of mica, &c., by a process of washing, they yield the china-clay of commerce. In composition this varies between wide limits; but in many instances it approximates to the kaolinite formula given above. Microscopical examination very rarely reveals the presence of any six-sided scales that can be definitely referred to the species kaolinite.

References.—J. A. Howe, A Handbook to the Collection of Kaolin, &c., in the Museum of Practical Geology, London, 1914; H. Ries, Clays, their Occurrence, Properties, and Uses, New York, 1908; A. B. Searle, An Introduction to British Clays, &c., London, 1912; G. Hickling, China-clay, its Nature and Origin, Trans. Manchester Geol. Mining Soc., 1908, 30, 334; H. Stremme, Die Chemie des Kaolins, Fortschritte Min. Krist. Petr. 1912, 2, 87; J. W. Mellor and A. D. Holdcroft, The Chemical Constitution of the Kaolinite Molecule, Trans. English Ceramic Soc. 1911, 10, 94; 1912, 11, 169; F. H. Butler, The Natural History of Kaolinite, Min. Mag. 1911, 16, 63; A. S. Watts, Mining and Treatment of Felspar and Kaolin in the Southern Appalachian Region, U.S. Bureau of Mines, 1913, Bull. 53. L. J. S.

KAPOK, strictly speaking, is the seed hair of *Eriodendron anfractuosum*, but the term is also applied to other vegetable downs. It is used as a stuffing for life-saving appliances at sea, due to its power of resisting the penetration of water owing to the peculiar structure of the fibre. In these appliances the kapok stuffing occupies about 15 c.c. per gram of fibre: a jacket containing 700 grams of stuffing represents a floating power of 10·5 kilos. After 72 hours in water with a weight of 9 kilos attached, this jacket still required 1·3 kilos more to submerge it; after 192 hours the weight required was 0·9 kilo. For the characteristics of the true kapok and of other substances classed under that name, *see* Cross & Bevan, J. Soc. Dyers and Col. 1910, 32, 274; J. Soc. Chem. Ind. 1917, 36, 79.

KAPOK OIL. Kapok oil is mainly derived from the seed kernels of *Eriodendron anfractuosum* (*Malvaceæ*), a tree which is common in the West Indies, Malay Archipelago, and various parts of Africa, but the commercial product is also obtained from the seeds of different species of bombax (*B. malabaricum*, *B. mexicanum*).

Kapok seeds are exported in large quantities, especially to Holland, where the oil is expressed and used for soap making, and, after refining, as an edible oil. The expressed oil, the yield of which is about 25 p.c. of the weight of the seeds, is of a greenish-yellow colour, and, like cotton seed oil, gives a deposit of 'stearine' when allowed to stand. From the analytical point of view the oil is of interest from the fact that it contains a constituent which gives the same coloration as cotton seed oil in Halphen's test. It may be distinguished from cotton seed oil, however, by its lower iodine value, and by its different behaviour in Milliau's modification of Bechi's test. The fatty acids are washed with cold water, rapidly dried at 105°, and shaken with an equal volume of a 1 p.c. solution of silver nitrate in absolute alcohol. Under these conditions the fatty acids from kapok oil give a deep brown coloration, whilst cotton seed oil fatty acids show only a slight brown tint.

The following values of genuine specimens of kapok and bombax oils are given by Sprinkmeyer and Diedrichs (Z. Nahr. Genussm. 1913, 26, 86, 450) :—

Oil	Sp.gr at 15°/15°	Ref Index (40), Zeiss	Iodine value	Acid value	Saponif. value
Kapok oil (Java, Ceylon, E. Africa, &c.) . . .	0·9235–0 9236	51 7–59·7	85·2–95·3	18 5–21·0	189·2–194·5
Bombax malabaricum . . .	0·9600	57 0	73 6	3·0	194·3
B. mexicanum . .	—	57 4	95 7	12·6	192·8

The fruit hairs both of kapok and bombax trees are used as upholstery material and especially as a filling material for lifebelts, but owing to their structure, are unsuitable for textile purposes (*cf.* Bull. Imperial Inst. 1920, 18, 335). C. A. M.

KATAMEN. Pyrazalone-phenyl-dimethyl sulphamino-benzoate.

KAURI-COPAL (-Bush Copal, -Gum or -Resin) is the solidified turpentine of the Kauri tree (*Dammara australis* [Steud.]) and occurs in great abundance in a fossil condition in various parts of New Zealand. It is dug up on the driest fern-hills as well as in the deepest swamps, but that from the latter is of inferior quality, as is also the gum obtained from the forks of living trees (J. Soc. Chem. Ind. 1893, 71 ; *ibid.* 1895, 528 ; *ibid.* 1898, 621 ; Bull. Imp. Inst. 1904, 2, 91). To obtain kauri-copal, it is first searched out a little below the surface by feeling for it with a steel-pointed piece of iron, after which it is dug out with an ordinary spade. It is then prepared for the market by scraping off the outer crust by hand, or better, by machinery (Eng. Pat. 17009 1890).

Four types of kauri-copal are known in commerce : (1) Pale kauri or fossil copal found in large masses varying from yellowish-white to clear yellow in colour, has an aromatic smell, brilliant fracture and can be pulverised to a white powder. It has sp.gr. 1·036, m.p. 165°, acid value 70·9, saponification value 73. (2) Brown kauri fossil copal is of a yellow-brown or deep yellow colour. It is difficult to powder, has a conchoidal fracture and an aromatic camphor-like odour. It has sp.gr. 1·053 ; m.p. 185°, acid value 78·8, saponification value 89·7. (3) Bush kauri is obtained at the foot of trees in irregular amber-like masses. It can readily be reduced to a yellow powder with an aromatic odour, and has sp.gr. 1·03, m.p. 150°, acid value 83·1, saponification value 78·5. (4) Bush kauri gathered from the tree itself has a vitreous fracture ; sp.gr. 1·038, m.p. 125°, acid value 81·8, saponification value 87 (Coffignier, Bull. Soc. chim. 1909, 5, 289 ; *see* also Tschirsch and Niederstadt, Arch. Pharm. 1901, 239, 145 ; Worstall, J. Amer. Chem. Soc. 1903, 25, 860). The various kinds of kauri differ in their solubilities in organic solvents, but all of them are only very slightly soluble in turpentine and more readily so in alcohol (Coffignier, *l.c.*). They are all almost completely soluble in amyl alcohol, amyl acetate, benzaldehyde, or aniline.

Kauri-copal is readily attacked by chlorine, bromine, or concentrated nitric acid (Muir, J. 1874, 923). On dry distillation it yields pinene and dipentene (Wallach, Annalen, 271, 309 ; Rennie, Chem. Soc. Trans. 1881, 240).

A recent fossil specimen of kauri-copal was found by Tschirsch and Niederstadt (*l.c.*) to consist of the following substances : 50 p.c. *a and β-kaurolic acids* $C_{12}H_{20}O_2$, m.p. 81°–83° and 85°–87° respectively (the *a*-acid yields a lead salt insoluble in alcohol, whereas the β-acid gives a soluble lead salt) ; 20 p.c. *kaurinolic* $C_{17}H_{34}O_2$, m.p. 128°–130°, and *kauronolic acids* $C_{12}H_{24}O_2$, m.p. 86°–89° (all these acids are monobasic and give a monoiodide), 12·0 p.c. *kauroresene* a light yellow indifferent substance, m.p. 63°–65° and not volatile in steam ; 12·5 p.c. of an ethereal essential oil, b.p. 150°–160°, sp.gr. 0·835 at 15° ; 1·5 p.c. *kauric acid* $C_{10}H_{16}O_2$, m.p. 192°, forming microscopic crystals $[a]_D$ +51·66°. It is a monobasic acid, yielding an iodine number corresponding to a monoiodide and a potassium and lead salt. Only about 2 p.c. of carbon was left on distillation of the kauri-copal (*see* also Thomson, Annalen, 1843, 47, 354). Kauri gum is used in the manufacture of oil varnishes, as an ingredient of the cement for linoleum manufacture, and also for dressing glazed calico. The transparent and semitransparent varieties are employed as substitutes for amber in the manufacture of mouthpieces for cigar-holders, pipes, &c.

The commercial product often contains as an admixture dammar resin, which is a much cheaper substance. Whether the kauri contains the latter can be determined rapidly in the following way: 0·5 gram of the finely ground sample is stirred up with chloroform in a porcelain crucible. It is then filtered through a small filter into a test tube, washed once and absolute alcohol added to the filtrate, when if the sample is pure kauri, the solution will remain clear, whereas if dammar is present a cloudiness or a precipitate will appear, according to the amount (Stewart, J. Soc. Chem. Ind. 1909, 349).

KAWA. The peeled dried rhizome of *Piper methysticum* (Forst. *fil*). Contains a resin which by treatment with caustic soda solution gives, on cooling, sodium kawaate. The corresponding acid, $C_{13}H_{12}O_3$, yellow needles, m.p. 164°–165°, appears to be either α or γ-cinnamylidenacetoacetic acid, probably the latter (Borsche and Roth, Ber. 1921, 54, 2229).

KAYA OIL. Kaya oil is obtained from the kernels of the nuts of a Japanese tree, *Torreya nucifera* (*Taxaceæ*), and when separated by cold expression is used as an edible oil. For the preparation of the commercial oil the seeds are crushed, steamed, and pressed while hot. Kaya oil has good drying properties, and is used as a lamp oil, and in the manufacture of paper. A specimen of the cold-drawn oil examined by Tsujimoto had the following characteristics: sp.gr. 0·9236; saponification value, 188·4; Hehner value, 95·7; and iodine value, 142·2. When brominated the fatty acids yield linolic tetrabromide. C. A. M.

KEENE'S CEMENT *v.* CALCIUM.

KELP *v.* IODINE.

KEPHALDOL. A pharmaceutical preparation of phenetidine, salicylic and citric acids.

KEPHIR *v.* MILK.

KERACYANIN *v.* ANTHOCYANINS.

KERAMYL. An aqueous solution of commercial hydrofluosilicic acid used as a disinfectant.

KERATIN is the principal constituent of the epidermis, hair, nails, hoofs, horns, wool, feathers, the skin of egg shells, &c. (Hedin, Zeitsch. physiol. Chem. 1894, 20, 186; Mohr, *ibid.* 1895, 20, 403; Abderhalden, *ibid.* 1905, 46, 31, 40; *ibid.* 48, 530, 535; *ibid.* 1907, 52, 348; *ibid.* 1908, 57, 339; Breinl and Baudisch, *ibid.* 1907, 52, 159; Friedmann, Chem. Zentr. 1903, i. 15).

It can be prepared from any of these substances by treating them successively with ether, alcohol, water, and dilute acids, or successively with artificial gastric juice, artificial pancreatic juice, boiling alcohol and boiling ether, keratin remaining as a residue, after removal of the fat and protein. Keratin is an albuminoid or sclero-protein, rich in sulphur (Bibra, Annalen, 96, 292; Raikow, Chem. Zeit. 1905, 29, 900; Baudisch, *ibid.* 1908, 32, 620), and like the other members of this class of substances, it is insoluble in all neutral solvents. When treated with concentrated alkalis it swells and dissolves on warming, but it is more sparingly soluble in dilute acids.

When boiled with acids and generally on hydrolysis, it yields a variety of decomposition products amongst which may be mentioned leucine, crystine, glycine, tyrosine, aspartic, and glutamic acids, alanine, arginine, &c., the relative quantities of the products as well as their nature depending on the source of the keratin (*see* above references; also Bleunard, Ann. Chim. Phys. 1882, [v.] 26, 40). Keratin is not acted on by pepsin and trypsin. When treated with hydrogen peroxide it gives sulphur, ammonia, sulphuretted hydrogen, carbon dioxide, acetaldehyde, and nitric, sulphuric, acetic, oxalic, succinic, and a small quantity of aromatic amino acids (Brienl and Baudisch, *l.c.*). On oxidation by potassium permanganate, the bulk of the sulphur remains as a water-soluble organic compound: 10 p.c. is split off as H_2SO_4 (Lissizin, Biochem. Bull. 1915, 18). According to Lissizin (Zeitsch. physiol. Chem. 1909, 62, 226), azelaic acid is also an oxidation product of keratin. Keratin gives Millon's protein reaction and a yellow colour with nitric acid, this being the origin of the yellow colour when nitric acid comes in contact with the skin. Keratin has been converted into useful products which can be used instead of casein for many purposes, by treating horn scraps, hair, &c., with 15 p.c. hydrochloric acid at ordinary temperature. After 10 days the liquid is decanted, the residue washed with water, digested with 6 p.c. sodium hydroxide solution for 24 hours; potassium permanganate is then added and after standing for 12 hours the residue is washed and subjected to a pressure of 400 atmospheres (Eng. Pat. 360895; J. Soc. Chem. Ind. 1906, 548).

Keratin or keratin substances can be converted into digestible albumoses and peptones containing sulphur by treatment with dilute mineral acids at moderate temperatures. These are isolated when a diluted sample, after treatment with phosphotungstic acid or other reagent for albumoses, gives a filtrate containing but little amino acid (U.S. Pat. 926909, 1909). By digesting horn for 14 days with $\frac{N}{2}$NaOH at 40°C. it is completely dissolved: on neutralising, H_2S is evolved and a precipitate formed. From the filtrate, a protalbumose is precipitated by saturation with salt. The filtrate deposits deutero-keratose on acidifying it (Langecker, Zeitsch. physiol. Chem., 108, 230).

Atmidkeratin and *atmidkeratose* are the products obtained when keratin is acted on by superheated steam; the gaseous products of this reaction being sulphuretted hydrogen and methyl mercaptan (Bauer, Zeitsch. physiol. Chem. 1902, 35, 343; *see* also Krukenberg, Jahrb. Thierchem. 1886, 27). Thermoplastic keratin compounds have been obtained by mixing intimately keratin with β-naphthol and subjecting the mixture to heat and pressure (U.S. Pat. 922692; J. Soc. Chem. Ind. 1909, 721).

KERMES. Kermes is the most ancient dyestuff on record, for it was known in the time o Moses, and is mentioned in Scripture by it Hebrew name, 'tola' or 'tolaschani.' Accordin to Tychsen (Bancroft's Philosophy of Permanen Colours, 1, 394), 'the scarlet or kermes dye wa known in the East in the earliest ages befor Moses, and was a discovery of Phœnicians i Palestine, but certainly not of the small wande ing Hebrew tribes.' Under the name 'coccus it is frequently referred to by the Greek an Latin writers.

Kermes is an insect found on the oak kermes (*Quercus coccifera*, Linn.), and when living the female insects, which are fixed to the twigs of the tree, resemble bluish berries, and are covered with a whitish powder. As soon as their eggs are on the point of hatching these insects should be collected, killed by exposure to the steam of vinegar, and dried, and the product has then the appearance of pale reddish-brown grains According to Bancroft, it would require 10 or 12 lbs. of kermes to produce the effect of a single lb. of cochineal.

Kermesic acid $C_{18}H_{12}O_9$, the colouring matter of kermes, was first isolated, in the crystalline condition, by Heisse (Arbeit. a. d. K. Gesundheitsamte, 1895, 513), and has since been examined by Dimroth (Ber. 1910, 43, 1387; and Annalen, 1913, 399, 43). To isolate the kermesic acid, the kermes is first extracted with ether to remove wax, and this has been examined by Dimroth and Sherndal (Annalen, 1913, 399, 43), and identified as ceryl cerotate $C_{52}H_{104}O_2$. The residue is then allowed to stand overnight with an ethereal solution of hydrochloric acid, by which means the kermesic acid, which exists in kermes in the form of a salt, is liberated and made capable of removal by repeated extraction with ether. For the purification of the substance, it is converted into its sparingly soluble sodium salt, which allows of its separation from *flavo-kermesic acid*,—a substance stated by Dimroth to be present in kermes dye to the extent of about 0·06 p.c.—the sodium salt of this being soluble in hot 2N sodium acetate solution, whereas the disodium salt of kermesic acid is almost insoluble. The sodium salt when dissolved in boiling sodium hydroxide solution and treated, whilst boiling, with excess of hydrochloric acid, yields a crystalline precipitate of kermesic acid.

Thus obtained, the acid consists of brick-red needles which decompose, without melting, at about 250°. It is distinguished from carminic acid by the fact that it is soluble in ether, and is much more sparingly soluble in cold water. On the other hand, the colour of the alkaline solutions of both colouring matters is practically identical. Kermesic acid is soluble, without decomposition, in concentrated sulphuric acid giving a violet-red solution, which, on addition of boric acid, becomes clear blue—if flavo-kermesic acid is present as impurity only a dull bluish-violet results.

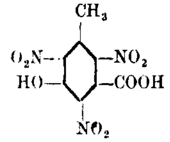
Disodium kermesate $C_{18}H_{10}O_9Na_2$, prepared by means of sodium acetate, consists of a red-brown crystalline powder, sparingly soluble in water with a violet-red colour.

Barium kermesate $(C_{18}H_{11}O_9)_2Ba$, is brown and contains water of crystallisation.

Tetra-acetyl kermesic acid $C_{18}H_8O_9(C_2H_3O)_4$, yellow needles, melts at 245°. *Kermesic acid trimethyl ether* $C_{21}H_{18}O_9$, orange-red needles, m.p. 310°, dissolves in sulphuric acid with a violet colour, and is prepared from the potassium salt by means of methyl sulphate in the presence of boiling toluene.

Flavo-kermesic acid $C_{13}H_8O_6$ crystallises in needles, or prisms, and differs considerably from kermesic acid in its dyeing properties and in the colour of its solutions.

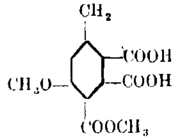
Kermesic acid is decomposed by warm concentrated nitric acid yielding *nitro-coccusic acid* (trinitro-cresotinic acid), identical with the acid



obtained in a similar way from carminic acid.

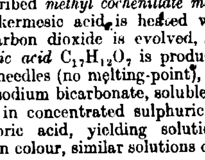
Kermesic acid contains no methoxy groups, and treatment with hydriodic acid gives the reduction product $C_{18}H_{12}O_8$, which decomposes at 275°.

When oxidised with hot potassium permanganate, kermesic acid trimethyl ether produces two products, the one being *methylcochenillate monomethyl ether*



which melts at 178°–180°, with formation of the anhydride, m.p. 149°. Digestion with boiling potassium hydroxide (25 p.c.) solution converts this ester into *cochenillic acid methyl ether* $C_{11}H_{10}O_7$, m.p. 200° (decomposition), whilst complete demethylation of ester, or acid, by means of hydriodic acid, yields hydroxyuvitic acid.

The second product of the oxidation is the *dimethyl ether* of *cresotinglyoxyl-dicarboxylic acid*



m.p. 108°–110° if anhydrous. The hydrated acid has m.p. 86°, and this, by oxidation with alkaline permanganate, is converted into the above-described *methyl cochenillate methyl ether.*

When kermesic acid is heated with water at 150°, carbon dioxide is evolved, and *dicarboxykermesic acid* $C_{17}H_{12}O_7$ is produced. This forms red needles (no melting-point), almost insoluble in sodium bicarbonate, soluble in caustic soda, and in concentrated sulphuric acid containing boric acid, yielding solutions which resemble, in colour, similar solutions of kermesic acid.

Bromination of kermesic acid yields (i) in boiling 50 p.c. acetic acid, *a-bromocarmin*; (ii) in boiling glacial acetic acid, *bromococcin* $C_{16}H_9O_8Br$; (iii) in methyl alcohol, followed by treatment with concentrated hydrobromic acid, *tribromococcin* $C_{16}H_7O_8Br_3$. (This product is also obtained when bromococcin is treated in the same way.)

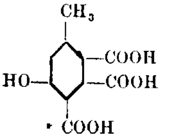
Bromococcin $C_{16}H_9O_8Br$ crystallises in red needles, m.p. 259°–260° (decomposition); it yields an acid potassium salt

$$C_{16}H_9O_8Br{\cdot}C_{16}H_8O_8BrK$$

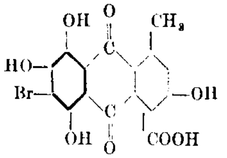
and a tetra-acetyl derivative

$C_{15}H_5O_8Br(CH_3CO)_4$,

which forms yellow crystals. When oxidised by means of warm alkaline hydrogen peroxide, in the presence of a catalyst, bromococcin yields cochenillic acid



and from these facts Dimroth and Scheurer conclude that bromococcin has the structure



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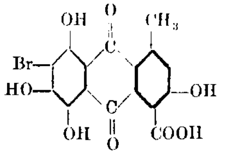
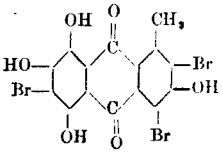


either of which is in agreement with the fact that, in respect of its dyeing properties, it resembles purpurin, not anthragallol.

Tribromococcin is formulated as either



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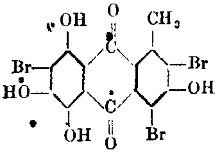


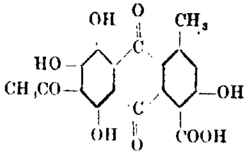
It crystallises from acetic acid in long red needles, m.p. 245°–248°, is soluble in concentrated sulphuric acid giving a red-violet solution, the colour of which changes to deep blue when boric acid is added.

Tetra-acetyl-tribromococcin

$C_{15}H_3O_8Br(CH_3CO)_4$

crystallises in green-yellow needles, m.p. 223°; it yields nitro-coccusic acid when treated with fuming nitric acid.

Dimroth and Scheurer point out the close relationship that exists between bromococcin and kermesic acid, and assign to the latter the structure



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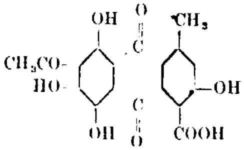
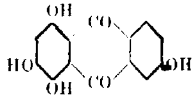


They support this by the results of the distillation of kermesic acid with zinc-dust, whereby they obtained α-methyl-anthracene (and from it prepared α-methyl-anthraquinone). They also consider it probable that anthracene is simultaneously produced.

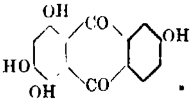
Dimroth and Fick (A. 1916, 411, 315) have shown that the latter of these two formulæ represents the correct constitution of kermesic acid.

They arrive at this from a comparison of hydroxyanthrapurpurine (1) and hydroxyflavopurpurine (2), obtained respectively from anthrapurpurine and flavopurpurine by means of sodium nitrite, boric acid and sulphuric acid.

(1)

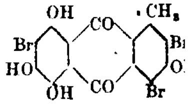


(2)



Thus as regards dyeing properties an absorption spectra hydroxyflavopurpurine an hydroxyanthrapurpurine differ sharply, an the latter only agrees with decarboxykermesic acid in these respects.

Also hydroxyanthrapurpurine when brominated under the conditions by which kermesic acid yields tribromococcin forms a tribromohydroxyanthrapurpurine. This shows a complete analogy to tribromococcin which must therefore be 2 : 4 : 7 tribromo-3 : 5 : 6 : 8-tetrahydroxy 1-methylanthraquinone.



Kermesic acid is thus closely related to carminic acid, which has been shown by Dimroth and Kämmerer (Ber. 1920, 53, 471) to differ from it only by possessing a side chain $C_6H_{11}O_5$ in place of the acetyl group.

Dyeing properties.—According to Hellot (Bancroft, Philosophy of Permanent Colours, 1, 404), 'the red draperies of the figures exhibited in the ancient Brussels and other Flemish tapestries were all dyed with kermes.' 'The fine red or crimson colour of those tapestries, which was originally called simply scarlet, took the name of *Venetian scarlet*, after the cochineal scarlet upon a tin base was discovered. . . .'

For the production of this scarlet, the wool, previous to dyeing, was mordanted with alum and tartar; and, according to Bancroft, there is no evidence even in more recent years of the employment of a tin mordant in respect of this colouring matter, although the experiments he carried out indicated that by this latter method a scarlet could be produced 'in every respect as beautiful and estimable as any which can be dyed with cochineal.' A. G. P.

KERMESITE. *Red antimony. Antimony blende, Pyrantimonite. Pyrostibite.* An oxysulphide of antimony formed by the oxidation of antimony sulphide, and occurring associated with grey and white antimony in Hungary, Saxony, Dauphiné, &c. Found in monoclinic crystals or in capillary tufts of six-sided prisms, of a cherry-red colour and adamantine lustre. Composition $Sb_2O_3{\cdot}2Sb_2S_3$ (*v.* ANTIMONY).

KEROSENE or **KEROSINE** *v.* PETROLEUM.

KETENES. A series of compounds containing the group $>C:CO$. They were discovered in 1905 by Staudinger, the first member to be isolated being diphenylketene $(C_6H_5)_2C:CO$. Ketenes may be prepared: (i) by the action of zinc on the chloride or bromide of an α-halogen substituted fatty acid; or (ii) by the action of heat on the anhydride of a dibasic acid. The ketenes are very reactive substances, and may be divided into two groups:—

I. *Aldo-ketenes.* These consist of ketene itself, monoalkyl derivatives and carbon suboxide. They are colourless and do not undergo auto-oxidation. They are polymerised by pyridine and quinoline, and do not form additive compounds with substances containing the $>C:O$ and $>C:N$— groups.

II. *Keto-ketenes.* The dialkyl derivatives of ketene belong to this group. They are coloured substances, and readily undergo auto-oxidation. They yield ketone bases with pyridine and quinoline, and form additive compounds with substances containing the $>C:O$ and $>C:N$— groups, such as quinone and benzylidineaniline.

Both groups combine readily with water, alcohols, and amines, and also with chlorine and bromine (Staudinger and Klever, Ber. 1908, 41, 906).

Ketene $H_2C:CO$. Discovered by Wilsmore and Stewart, who obtained it by the action of a heated platinum wire on the vapour of acetic anhydride. The gaseous products were liquefied, and then submitted to fractional distillation (Nature, 1907, 75, 510; Chem. Soc. Trans. 1907, 1938). Schmidlin and Bergman (Ber. 1910, 43, 2821) obtained a 14 p.c. yield of ketene by passing the vapour of acetone through a hard glass tube filled with porous earthenware, heated at 500°–600°. It may also be prepared by the action of zinc on bromacetyl bromide in ethyl acetate. The products of the reaction are rapidly distilled, the ketene being removed from the warm solvent in a current of hydrogen, condensed in liquid air, and freed from traces of ethyl acetate by repeated fractionation at −60° (Staudinger and Klever, Ber. 1908, 41, 594). By the last method the yield of ketene from bromacetyl bromide is 7–13 p.c.; from bromacetyl chloride 3–4 p.c.; from chloracetyl chloride or chloracetyl bromide *nil* (Staudinger and Kubinsky, Ber. 1909, 42, 4213).

Ketene is a colourless liquid, b.p. −56°, and can be solidified to a mass of colourless crystals, m.p. −151°. It has a very penetrating odour, and its vapour attacks the mucous membrane. It combines with water, alcohol, aniline, &c., to form acetic acid, ethyl acetate, and acetanilide respectively, and with bromine in ethereal solution to form bromacetyl bromide. Liquid hydrogen chloride and sulphuretted hydrogen at the ordinary temperature yield acetyl chloride and thioacetic anhydride. When it reacts with water no trace of glycollic aldehyde is produced, and for this and other reasons, ketene is represented as $H_2C:CO$ and not as $CH:C{\cdot}OH$ (Staudinger and Klever, *l.c.*; Chick and Wilsmore, Chem. Soc. Proc. 1908, 77). It does not give an additive compound with quinone, nor ketene bases with pyridine and quinoline. Metallic chlorides and tertiary bases induce polymerisation to a dark-coloured liquid, this change also taking place when ketene is kept for some time. The chief constituent of this polymeride is a colourless liquid of pungent odour, b.p. 126°–127°, and when frozen, m.p. −6° to −7°. It has the formula $C_4H_4O_2$, and hence is formed by the condensation of two molecules of ketene. It combines with water and aniline to form acetoacetic acid and acetoacetanilide respectively, but only combines with alcohol to produce ethyl acetoacetate on addition of a trace of acid. On standing in sealed tubes, or by the addition of pyridine, dehydracetic acid is formed. Hence this substance may be acetylketene $CH_3COCH:CO$ or Δ′-*cyclo*butene-1-ol-3-one $CO<\begin{smallmatrix}CH_2\\CH\end{smallmatrix}\geqslant C{\cdot}OH$, the semi-enol of *cyclo*butane-1:3-dione. The action of bromine was found to result in the formation of a γ- derivative $CH_2<\begin{smallmatrix}COBr\\COCH_2Br\end{smallmatrix}$ and not an α- derivative, $CH_3CO{\cdot}CHBr{\cdot}COBr$, thus proving it to have the latter configuration (Chick and Wilsmore, Chem. Soc. Trans. 1908, 946; 1909, 1978; *cf.* Staudinger and Bereza, Ber. 1909, 42, 4908).

Methyl ketene $CH_3{\cdot}CH:CO$. Obtained in dilute ethereal solution by the action of zinc on an ethereal solution of α-bromopropionyl bromide.

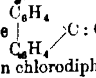
Ethyl ketene $C_2H_5{\cdot}CH:CO$. Similarly from α-bromobutyl bromide.

Carbon suboxide $O:C:C:C:O$. Obtained by action of zinc on dibromomalonyl bromide *v.* CARBON SUBOXIDE.

Dimethyl ketene $(CH_3)_2C:CO$. Prepared by the action of zinc on a solution of α-bromo*iso*butyl bromide in ethyl acetate, and distilling the resulting product under 15–16 mm. at −20° (Staudinger and Klever, Ber. 1906, 39, 968). Also by heating dimethylmalonic anhydride under 12 mm. pressure at 160°–180° (Staudinger and Ott, Ber. 1908, 41, 2208). It is a mobile yellow liquid, b.p. 48·5° (12 mm.); m.p. −97·5°; stable at −20° under atmospheric pressure, but at ordinary temperature polymerises to a colourless substance, m.p. 112°, apparently the diketone $(C\cdot(CH_3)_2CO)_2$. Water converts dimethylketene into *iso*butyric acid, and it undergoes the other reactions common to the keto-ketenes. Dimethylketene bases *v.* Staudinger, Klever, and Kober, Annalen, 1910, 374, 1. In the preparation of this ketene a liquid polymeride $(C_4H_6O)_2$, b.p. 170°–171°, having an odour of peppermint, is also formed (Staudinger and Klever, Ber. 1907, 40, 1149).

Diethylketene $(C_2H_5)_2C:CO$. Prepared by heating diethylmalonic anhydride under 12 mm. pressure at 160°–180°. It forms a yellow liquid, b.p. 91°–92° (749 mm.), solidifying to a mass of yellow crystals in liquid air (Staudinger and Ott, *l.c.*).

Diphenylketene $(C_6H_5)_2C:CO$. Prepared by the action of zinc on diphenylchloracetyl chloride in ethereal solution (Staudinger, Ber. 1905, 38, 1735); by the action of tertiary bases on diphenylacetyl chloride (Ber. 1907, 40, 1145); or by the interaction of benzil and hydrazine, oxidation of the hydrazibenzil, and warming the azibenzil to 60° (Curtius, Ber. 1889, 2161; J. pr. Chem. [ii.] 4, 182; Schroeter, Ber. 1909, 2346). It is a liquid having the colour of a concentrated solution of potassium dichromate, and solidifies in a freezing mixture to a mass of yellow crystals; b.p. 146° (12 mm.). Water converts it into diphenylacetic acid, and it undergoes similar reactions to the other keto-ketenes. On exposure to air it becomes viscid, addition of light petroleum throwing out a white oxidation product. Dry hydrogen chloride passed into a benzene solution of the ketene yields diphenylacetylchloride, whilst a dilute solution of hydrochloric acid yields diphenyl acetic anhydride. It shows no tendency to polymerise, and treated with magnesium phenylbromide, yields triphenylvinyl alcohol. With quinone the β-lactone $O:C_6H_4\!<\!\begin{smallmatrix}C(C_6H_5)_2\\ O\end{smallmatrix}\!>\!CO$ is formed, and with benzylidine aniline the β-lactam $C(C_6H_5)_2\!<\!\begin{smallmatrix}CO\\ CH(C_6H_5)\end{smallmatrix}\!>\!N\cdot C_6H_5$. The former, on heating, yields compounds of the type of diphenylquinomethane and tetraphenylquinodimethane, and the latter acylic fulvenes (Staudinger, Ber. 1908, 41, 1355, 1493).



Diphenylene ketene $\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\!>\!C:CO$. Prepared by the action of zinc on chlorodiphenylene acetyl chloride (from phosphorus pentachloride and diphenyleneglycollic acid) in ether in absence of air and moisture. It forms red crystals, m.p. 90° to a red liquid, decomposing at 150°; gives an indigo-blue colour with sulphuric acid. With excess of water diphenylene acetic acid is formed, and with the requisite quantity diphenylene acetic anhydride. It undergoes the usual reactions (Staudinger, Ber. 1906, 39, 3062).

Ethylketene carboxylate

$$CO:C(C_2H_5)\cdot CO_2\cdot C_2H_5$$

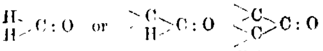
An ethereal solution of ethylbromomethylmalonate chloride $C_2H_5\cdot CBr\!<\!\begin{smallmatrix}CO_2C_2H_5\\ COCl\end{smallmatrix}$ reacts with zinc, producing ethylketenecarboxylate, which rapidly polymerises into 1 : 3-diethyl *cyclo*butane-2 : 4-dione-1 : 3-dicarboxylate

$$C_2H_5O_2C\cdot C(C_2H_5)\!<\!\begin{smallmatrix}CO\\ CO\end{smallmatrix}\!>\!C(C_2H_5)CO_2C_2H_5$$

This, on heating at 180°–200°, yields the ketene as a colourless liquid, b.p. 48° (15 mm.), m.p. 57·8° (Staudinger and Bereza, Ber. 1909, 42, 4908).

KETOHYDRINDENE *v.* INDENE.

KETONES. The ketones are a class of organic compounds characterised by the presence of the carbonyl group $>C:O$, united by each of its valencies to carbon. They are differentiated in this way from the aldehydes which contain the carbonyl group united on the one hand to hydrogen, and on the other to hydrogen or carbon. The characteristic groupings of aldehydes and ketones are shown as follows:—



Aldehydes Ketones

Ketones proper have hydrocarbon radicles or simple derivatives thereof (substituted by halogens, &c.) united with the carbonyl group, but a large number of other compounds of ketonic character are known, such as the keto-alcohols (*e.g.* $CH_3\cdot CO\cdot CH_2OH$), and the ketonic acids (*e.g.* $CH_3\cdot CO\cdot CO_2H$). Such compounds, besides showing specific properties due to the presence of the carbinol or carboxyl groups, also exhibit ketonic reactions due to the presence of the carbonyl group.

Ketones may be classified according to the number of carbonyl groups into *simple ketones*, *diketones*, &c., whilst, according to the radicles united with the carbonyl, they may be separated into *aliphatic*, *aromatic*, and *mixed ketones*.

Another type of ketone is furnished by those compounds in which the carbon atom of the carbonyl group is a member of a closed ring; such *cyclic ketones*, in which the carbon chain is saturated, closely resemble the aliphatic ketones in their properties. Unsaturated cyclic ketones also exist; one class, the quinones, will be treated separately, as they possess many distinctive properties not shared by the other ketones.

Respecting the nomenclature of the ketones, a few are known by trivial names, *e.g.* acetone, benzophenone, acetophenone, &c., but usually a more systematic nomenclature is adopted. This may refer either to the radicles attached to the carbonyl group, or to the position of the carbonyl groups in the chain. Acetone $CH_3\cdot CO\cdot CH_3$ may be more systematically termed dimethylketone or propanone; benzophenone $C_6H_5\cdot CO\cdot C_6H_5$ diphenylketone or diphenylmethanone; and acetophenone $C_6H_5\cdot CO\cdot CH_3$ phenyl methyl ketone or ethylphenone.

Whilst for simple ketones the second systematic nomenclature, that recommended by the Geneva Congress, has no striking advantages; in the case of polyketones it is very useful, as it enables the trivial names given to various substances to be replaced and rational names to be given to new compounds as they are discovered. Thus diacetyl becomes butane-dione, acetylacetone is pentane-2 : 4-dione, and is thus completely differentiated from acetylpropional which is pentane-2 : 3-dione.

OPEN CHAIN MONOKETONES.

Preparation.—(1) By addition of water to hydrocarbons of the type $R{\cdot}C{:}C{\cdot}H$: thus allylene, if led into an aqueous solution of mercuric chloride at 90°–95°, yields acetone (Kutscherow, Ber. 1884, 17, 15)

$$CH_3{\cdot}C{:}CH + H_2O = CH_3{\cdot}CO{\cdot}CH_3$$

Béhal and Desgrez find that hydrocarbons of the formula C_nH_{2n-2} add the elements of acetic acid at 280°, the addition products being decomposed by water with formation of ketones.

(2) Secondary alcohols are directly oxidised to ketones. The use of manganic salts for this purpose has been patented by W. Lang (D. R. P. 166357). Ketones may also be obtained from secondary alcohols by passing their vapours over heated, finely divided copper (P. Sabatier and J. B. Senderens, Ann. Chim. 1905 [viii.] 4, 433).

(3) Primary alcohols of the type

$$CHRR'{\cdot}CH_2OH$$

give formic acid and a ketone on oxidation (Kannonikow and Saytzew, Annalen, 1875, 175, 377):

$$CH(CH_3)(C_2H_5)CH_2OH + 3O \\ = CH_3{\cdot}CO{\cdot}C_2H_5 + H{\cdot}CO_2H + H_2O$$

(4) Hydrolysis of some halogen compounds which might be expected to yield unsaturated tertiary alcohols furnishes ketones in their place:

$$CH_3{\cdot}CCl : CH_2 \rightarrow (CH_3{\cdot}C(OH) : CH_2) \\ \rightarrow CH_3{\cdot}CO{\cdot}CH_3$$

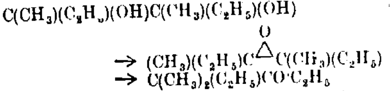
(Oppenheim, Annalen, 1868, Spl. 6, 365).

It has also been found that certain chlorhydrins when heated with water under pressure, yield ketones instead of glycols:

$$C(CH_3)_2(OH)CH(CH_3)Cl \\ = CH(CH_3)_2CO{\cdot}CH_3 + HCl$$

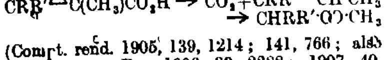
(K. Krassusky, J. Russ. Phys. Chem. Soc. 1901, 33, 791; 1902, 34, 287).

(5) On warming pinacones (ditertiary glycols) with dilute acids pinacolines (ketones containing a tertiary alkyl radicle) are produced:



$$C(CH_3)(C_2H_5)(OH)C(CH_3)(C_2H_5)(OH) \\ \rightarrow (CH_3)(C_2H_5)C\overset{O}{\triangle}C(CH_3)(C_2H_5) \\ \rightarrow C(CH_3)_2(C_2H_5)CO{\cdot}C_2H_5$$

The mechanism of the reaction discovered by G. Darzens is probably similar. Ethyl α-chloropropionate condenses with ketones $R{\cdot}CO{\cdot}R'$ to form αβ-trisubstituted glycidic esters of the general type $CRR'\overset{O}{\triangle}C(CH_3)CO_2C_2H_5$. When these are hydrolysed the unstable acid loses carbon dioxide, and the oxide isomerises to a ketone



$$CRR'\overset{O}{\triangle}C(CH_3)CO_2H \rightarrow CO_2 + CRR'\overset{O}{\triangle}CH{\cdot}CH_3 \\ \rightarrow CHRR'{\cdot}CO{\cdot}CH_3$$

(Compt. rend. 1905, 139, 1214; 141, 766; also R. Stoermer, Ber. 1906, 39, 2288; 1907, 40, 488; M. Tiffeneau and Dorlencourt, Compt. rend. 1906, 143, 126; Ann. Chim. 1907, [viii.] 10, 322; Delacre, Bull. Soc. chim. 1911, [iv.] 9, 1024; Parry, Chem. Soc. Trans. 1915, 107, 108).

Changes of the types

$$\left.\begin{array}{r} HO{\cdot}CRR'{\cdot}CRR'{\cdot}OH \searrow \\ HO{\cdot}CR_2{\cdot}CR_2'{\cdot}OH \nearrow \end{array}\right. R'{\cdot}CO{\cdot}CR_2R'$$

have attracted much attention (A. Orékhoff, Bull. Soc. chim. 1919, [iv.] 25, 9, 108, 111, 115, 174, 179, 182, 186; Tiffeneau and Orékhoff, Compt. rend. 1920, 171, 400, 473; 1921, 172, 387; Bull. Soc. chim. 1921, [iv.] 29, 422, 445, 809; Billard, Bull. Soc. chim. 1921, [iv.] 29, 429; Lévy, *ibid.*, 820). Pinacolines of the type $CR_3{\cdot}CO{\cdot}R'$ cannot exhibit tautomerism, but when one of the groups R is replaced by H, tautomeric change is possible so that the compound produced by the action of aluminium chloride on trichloroacetyl chloride and benzene (Delane, Bull. Soc. chim. 1895, [iii.] 13, 857; Gardeur, Bull. Acad. roy. Belg. 1897, [iii.] 34, 67) may be triphenylethanone as originally formulated or possibly triphenylvinyl alcohol (Biltz, Ber. 1899, 32, 650; Annalen, 1897, 296, 242). The latter structure was accepted on many sides but Kohler (Amer. Chem. J. 1906, 36, 177), Orékhoff (Bull. Soc. chim. 1919, [iv.] 25, 9, 186) and Meyer and Gottlieb-Billroth (Ber. 1921, 54, 575) reverted to the ketonic formula. McKenzie and Boyle (Trans. Chem. Soc. 1921, 119, 1131) also think the substance is probably triphenylethanone having studied its reaction with phenyl magnesium bromide.

(6) By the dry distillation of the calcium or barium salts of acids

$$(R{\cdot}CO{\cdot}O)_2Ca = CaCO_3 + R{\cdot}CO{\cdot}R$$

The products obtained in this way are never pure; calcium acetate, for example, yields not only acetone, but also homologous ketones (R. Fittig, Annalen, 1859, 110, 17). When a mixture of the calcium salts of two acids is distilled together the separate ketones corresponding to each salt and their usual impurities are obtained, together with a greater or less yield of the mixed ketone.

The aliphatic acids are directly converted into ketones by heating with iron-filings or passing their vapours over heated aluminium, thorium, zirconium or uranium oxides

$$2R{\cdot}COOH = R{\cdot}CO{\cdot}R + CO_2 + H_2O$$

A number of other oxides can be used. Mailhe has employed zinc oxide and, more especially, cadmium oxide as a catalyst, whilst either ferrous or ferric oxide may be used at 430°–490° (W. Ipatiew, J. Russ. Phys. Chem. Soc. 1908, 40, 514; Ber. 1910, 43, 3383; J. B. Senderens, Compt. rend. 1909, 148, 297; 149, 995; 1910, 150, 111, 1336; 1911, 152, 384; Ann. Chim. 1913, [viii.] 28, 243; Bull. Soc. chim. 1914, [iv.] 15, 84; Easterfield and Taylor, Chem. Soc. Trans. 1911, 2298; Mailhe, Compt. rend. 1913, 157, 219; Bull. Soc. chim. 1913, [iv.] 13, 666).

Small amounts of acetone have been obtained by heating acetic anhydride to 290°–300° (Bamberger, Ber. 1910, 43, 3517).

Higher ketones, *e.g.* stearone, have been prepared from higher acids and catalysts (Schicht and Grün, D. R. PP. 295657, 296677).

(7) Ketones are obtained from tertiary

α-hydroxy acids either by oxidation (chromic acid) or by heating with mineral acids :

$$CRR'(OH)CO_2H+O=R{\cdot}CO{\cdot}R'+CO_2+H_2O$$

$$CRR'(OH)CO_2H =R{\cdot}CO{\cdot}R'+H{\cdot}CO_2H \text{ (or } H_2O+CO)$$

Since acids of the type $CRR'H{\cdot}CO_2H$ may be oxidised by alkaline permanganate to acids with the structure $CRR'(OH)CO_2H$, they might serve as a source of ketones ; in fact, electrolytic oxidation of *iso*butyric acid leads directly to acetone (M. Moest, D. R. P. 138442).

An analogous reaction is that by which the amides of α-bromo acids lose hydrogen bromide and cyanide on heating with aqueous or alcoholic sodium hydroxide, an aldehyde or a ketone being produced (G. Mossler, Monatsh. 1908, 29, 69) :

$$CRR'Br{\cdot}CO{\cdot}NH_2+2NaOH =R{\cdot}CO{\cdot}R'+NaCN+NaBr+2H_2O$$

Aldehydes and ketones are respectively obtained from amino acids $R{\cdot}CH(NH_2)CO_2H$ and $RR'C(NH_2)CO_2H$ by the action of hypochlorites :

$$RR'C(NH_2)CO_2H+HOCl=RR'C{:}O+CO_2+NH_4Cl$$

(K. Langheld, D. R. PP. 226226 and 226227).

(8) The β-ketocarboxylic acids, or their esters, undergo 'ketonic fission' on heating with dilute acids or alkalis (heating with concentrated alkaline solutions effects acid fission) :

$$R{\cdot}CO{\cdot}CHR'{\cdot}CO_2C_2H_5+H_2O =R{\cdot}CO{\cdot}CH_2R'+CO_2+C_2H_5OH$$

A simple method of effecting the ketonic fission of higher members of this series of esters by heating for a few minutes with sulphuric acid, pouring into water and distilling in a current of steam has been described by L. Bouveault and R. Locquin (Bull. Soc. chim. 1904, [iii.] 31, 1153 ; *cp.* Michael and Wolgast, Ber. 1909, 42, 3176).

(9) Ketones are produced by the interaction of acid chlorides and organo-metallic compounds (Freund, Annalen, 1861, 118, 1) :

$$2C_nH_{2n+1}{\cdot}COCl+Zn(C_mH_{2m+1})_2 =ZnCl_2+2C_nH_{2n+1}{\cdot}CO{\cdot}C_mH_{2m+1}$$

(10) Latterly magnesium alkyl halides (Grignard's reagents) have been largely applied to the synthesis of ketones. Nitriles yield imino derivatives, which are hydrolysed by dilute acids to ammonia and ketones (E. E. Blaise, Compt. rend. 1901, 132, 38 ; 133, 1217) :

$$R{\cdot}C{:}N+MgBrR'=RR'C:N{\cdot}MgBr$$

$$2RR'C:N{\cdot}MgBr+2H_2SO_4+2H_2O =MgBr_2+MgSO_4+(NH_4)_2SO_4+2RR'C:O$$

A similar reaction using the esters of α-bromo acids and zinc leads to the synthesis of β-ketonic esters

$$R{\cdot}C{:}N+Zn+CR'HBr{\cdot}CO_2C_2H_5 =BrZn{\cdot}N:CR{\cdot}CHR'{\cdot}CO_2C_2H_5$$

Ketones may also be obtained from cyanogen by the action of magnesium alkyl halides :

$$CN{\cdot}CN+Mg(C_2H_5)I=CN{\cdot}C(C_2H_5):N{\cdot}MgI$$

$$CN{\cdot}C(C_2H_5):NMgI+Mg(C_2H_5)I =MgI(CN)+C(C_2H_5)_2:N{\cdot}MgI$$

(11) Acid amides may be employed in place of nitriles (C. Béis, Compt. rend. 1903. 137. 575 ; Ryan and Nolan, Proc. Roy. Irish Acad. 1912, 30, B, 1) :

$$R{\cdot}CO{\cdot}NH_2+2MgR'X =CRR'(NHMgX)OMgX+R'H$$

$$CRR'(NHMgX(OMgX+2H_2O =NH_2{\cdot}CRR'{\cdot}OH+MgX_2+Mg(OH)_2$$

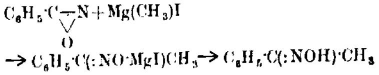
$$NH_2{\cdot}CRR'{\cdot}OH=R{\cdot}CO{\cdot}R'+NH_3$$

The yields obtained by this method vary from 20 to 50 p.c., increasing as the complexity of the radicle R increases.

Imino esters (*e.g.* $C_6H_5{\cdot}C({:}N{\cdot}C_6H_5){\cdot}OCH_3$) and imino chlorides may also be employed (R. Marquis, Compt. rend. 1906, 142, 711). whilst H. Fournier finds ketones amongst the products of the reactions between Grignard's reagents and acid anhydrides (Bull. Soc. chim. 1910, [iv.] 7, 836).

In certain cases ketones may be obtained by the action of organo-magnesium compounds on dried sodium salts, *e.g.* methyl *iso*butyl ketone from magnesium *iso*butyl bromide and sodium acetate (Salkind and Beburischwili, Ber. 1909, 42, 4500). For other syntheses involving organo-metallic compounds *v.* Blaise and Maire (Ann. Chim. 1908, [viii.] 15, 556 ; Barbier and Locquin, Bull. Soc. Chim. 1911, 9, 717, 722 ; Reynolds, Amer. Chem. J. 1911, 46, 198 ; Darzens a. Rost, Compt. rend. 1911, 153, 772).

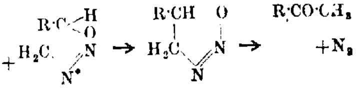
(12) The nitrile oxides yield ketones on reaction with magnesium alkyl halides. Thus benzonitrile-oxide and magnesium methyl iodide yield benzonitrile (by reduction), acetophenone, and its oxime :



$$C_6H_5{\cdot}C{=}N\,(O)+Mg(CH_3)I \rightarrow C_6H_5{\cdot}C({:}NO{\cdot}MgI)CH_3 \rightarrow C_6H_5{\cdot}C({:}NOH){\cdot}CH_3$$

(H. Wieland, Ber. 1907, 40, 1667).

(13) Ketones containing one methyl group can be obtained by the reaction of diazomethane with aldehydes. In this case it is probable that an unstable furodiazole is first produced, which breaks down into nitrogen and a ketone :



The method is of general applicability ; ketones may be obtained from *iso*valeraldehyde, benzaldehyde, &c., whilst trichloroacetone has been obtained in a pure condition by using chloral (Schlotterbeck, Ber. 1907, 40, 479, 1826, 3000 ; 1909, 42, 2559, 2565).

(14) In certain cases ketones may be converted into higher homologues by the action of sodamide and an alkyl halide. In this way diethyl ketone yields ethyl *iso*propyl ketone, di*iso*propyl ketone, and a compound $C_{15}H_{26}O$:

$$CH_3{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CH_3 \rightarrow (CH_3)_2CH{\cdot}CO{\cdot}CH_2{\cdot}CH_3 \rightarrow (CH_3)_2CH{\cdot}CO{\cdot}CH(CH_3)_2$$

(A. Haller and Bauer, Compt. rend. 1910, 150, 669 ; 1911, 153, 21, 1415 ; 1912, 154, 555 ; 1913, 156, 1499, 1295 ; Ann. Chim. 1913, [viii.] 29, 313 ; Zerner, Monatsh. 1911, 32, 677 ; Dumesnil, Ann. Chim. 1917, [ix.] 8, 70).

(15) Formaldehyde acts on ketones in presence of alkaline condensing agents, giving

keto alcohols, which may be dehydrated to unsaturated ketones (Farbenfab. vorm. Fr. Bayer & Co. D. R. PP. 222551 and 223207):

$$CH_3{\cdot}CO{\cdot}CH_3+CH_2O=CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2OH$$
$$=CH_3{\cdot}CO{\cdot}CH:CH_2+H_2O$$

Hydroxy ketones have also been obtained by the action of carbon monoxide on the Grignard reagents

$$2CO+2MgRX\rightarrow 2O:CR{\cdot}MgX$$
$$\rightarrow MgX{\cdot}O{\cdot}CR(MgX){\cdot}CR:O\rightarrow OH{\cdot}CHR{\cdot}CR:O$$

(Egorova, J. Russ. Phys. Chem. Soc. 1914, 46, 1319).

Saturated ketones can be prepared from ketones possessing ethylene linkages by reduction with hydrogen in presence of palladium or platinum (Skita and Meyer, Ber. 1912, 45, 3579, 3589; Vavon and Faillebin, Compt. rend. 1919, 169, 66).

The hydroxymethylene compounds obtained from ketones and formaldehyde can be reduced to saturated compounds by hydrogen in presence of a colloidal palladium catalyst. This is virtually a method of methylating a saturated ketone (J. D. Riedel, A. G., D. R. P. 266405; Kötz and Schaeffer, J. pr. Chem. 1913, [ii.] 88, 604).

(16) Aromatic ketones (also mixed ketones) can be obtained by the action of acid chlorides on aromatic hydrocarbons in presence of aluminium chloride, &c. (Friedel and Crafts, Ann. Chim. 1884, [vi.] 1, 507):

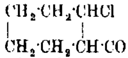
$$C_6H_6+CH_3{\cdot}CO{\cdot}Cl=CH_3{\cdot}CO{\cdot}C_6H_5+HCl$$

This reaction may sometimes extend to the aliphatic series: thus benzoyl chloride and ethylene react in presence of aluminium chloride to give phenyl vinyl ketone (Norris and Couch, J. Amer. Chem. Soc. 1920, 42, 2329).

Ketones in which both radicles attached to the carbonyl group are the same may be obtained by the action of carbonyl chloride on aromatic hydrocarbons in presence of aluminium chloride:

$$2C_6H_6+COCl_2=C_6H_5{\cdot}CO{\cdot}C_6H_5+2HCl$$

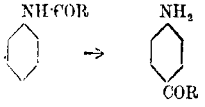
When acetyl chloride acts on a solution of *cyclo*hexene in carbon disulphide solution under the influence of aluminium chloride, an addition product



$$\begin{array}{l}CH_2{\cdot}CH_2{\cdot}CHCl\\ |\qquad\qquad\quad |\\ CH_2{\cdot}CH_2{\cdot}CH{\cdot}CO{\cdot}CH_3\end{array}$$

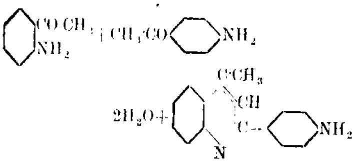
is formed, from which tertiary bases remove the elements of hydrogen chloride with production of tetrahydroacetophenone (Darzens, Compt. rend. 1910, 150, 707).

(17) The introduction of amino or hydroxyl groups renders aromatic nuclei still more liable to attack. Dimethylaminobenzoyl chloride and tetramethyldiaminobenzophenone (Michler's ketone) are successively produced by the reaction of phosgene with dimethylaniline, no condensing agent being necessary (Ber. 1876, 9, 715, 1900). *p*-Aminoacetophenone is formed by boiling 2 parts of aniline with 5 parts of acetic anhydride and 3 parts of zinc chloride for 4–5 hours (Klingel, Ber. 1885, 18, 2688); whilst 2:4-dihydroxyacetophenone (resacetophenone) is obtained when 2 parts of resorcinol and 3 parts each of acetic acid and zinc chloride are heated to 150° (Nencki and Sieber, J. pr. Chem. 1881, [ii.] 23, 147). Probably acyl derivatives are first formed which subsequently undergo isomerisation, *e.g.*:



For the mechanism of isomerisation of acyl anilides, *see* F. D. Chattaway (Chem. Soc. Trans. 1904, 85, 340, 386, 589, 1663; Angel, *ibid.* 1912, 101, 515).

The conversion of acetanilide into aminoacetophenone is of interest in connection with the formation of flavaniline, which may be obtained by several hours' heating at 250°–270° of 2 parts of acetanilide with 1 part of zinc chloride (O. Fischer and Rudolph, Ber. 1882, 15, 1500), or a mixture of *o*- and *p*-aminoacetophenones with zinc chloride at 90° (O. Fischer, Ber. 1886, 19, 1038).



An acyl group generally enters the aromatic nucleus para to a hydroxyl group, if the position is free. α-Naphthol, however, gives α-hydroxy-β-naphthyl methyl ketone, m.p. 103° (Friedlander, Ber. 1895, 28, 1946). Another modification, m.p. 98°, has been described (Torrey, J. Amer. Chem. Soc. 1910, 32, ii. 1477; *see* also Witt and Braun, Ber. 1914, 47, 3216).

Hydroxyketones can also be obtained by condensing phenols with nitriles in presence of hydrogen chloride (Hoesch, Ber. 1915, 48, 1122; Stephen, Trans. Chem. Soc. 1920, 117, 1529).

(18) Aromatic ketones may be obtained by the oxidation of diaryl methanes with chromic acid (Zincke, Annalen, 1871, 159, 377):

$$C_6H_5{\cdot}CH_2{\cdot}C_6H_5+2O=C_6H_5{\cdot}CO{\cdot}C_6H_5+H_2O$$

(19) Ketones (and aldehydes) are produced by the reduction of ozonides, particularly with potassium ferrocyanide, in presence or absence of acids (C. Harries, D.R.P. 321567).

General properties and reactions.—(1) The aliphatic ketones are generally liquid, the aromatic ketones solid at ordinary temperatures; usually they possess an ethereal or aromatic odour; most of them are insoluble in water, but dissolve easily in alcohol, ether, &c. They usually boil without decomposition: on passing the vapour of acetone over baked clay at 500°–600°, methane and ketene $CH_2:CO$ are produced (J. Schmidlin and M. Bergman, Ber. 1910, 43, 2821).

Metallic derivatives of ketones are known. Below 0°, acetone yields a sodium derivative

$$CH_3{\cdot}C(ONa):CH_2$$

from which an unsaturated tertiary alcohol may be obtained, by reaction with acetylene (Fr. Bayer & Co., Fr. Pat. 474745).

(2) Reduction of ketones by sodium amalgam

gives secondary alcohols, ditertiary glycols (pinacones) are formed at the same time :

$$CH_3{\cdot}CO{\cdot}CH_3+2H=CH_3{\cdot}CH(OH)CH_3$$
$$2CH_3{\cdot}CO{\cdot}CH_3+2H=(CH_3)_2C(OH)C(OH)(CH_3)_2$$

Pinacone may be obtained from acetone by reduction with sodium in presence of a liquid, such as ether, indifferent to sodium (B. A. S. F., D. R. P. 248252). Some ketones are reduced to pinacones when their alcoholic solutions are exposed to light (Cohen, Chem. Weekblad, 1916, 13, 590). Hydrogen in presence of platinum black gives secondary alcohols; the reaction is very general (Vavon, Compt. rend. 1912, 155, 286).

The reduction of ketones by aluminium or zinc amalgam in presence of 80 p.c. alcohol gives secondary alcohols and pinacones. With benzophenone, the formation of the pinacone is found to be favoured by a slight acid reaction; benzhydrol, on the other hand, by addition of ammonia (Böeseken and Cohen, Proc. K. Akad. Wetensch. Amsterdam, 1913, 16, 91; Cohen, Rec. trav. chim. 1919, 38, 72, 113; 1920, 39, 243; Montagne, *ibid.* 339, 350).

Fatty aromatic and aliphatic ketones are reduced to the corresponding hydrocarbons by heating with hydrochloric acid and amalgamated zinc (Clemmensen, Ber. 1913, 46, 1857; 1914, 47, 51, 681). The CO-group may be reduced to CH_2 by reducing hydrazones, &c (Wolff, Annalen, 1912, 394, 86).

The phytochemical reduction of ketones and diketones gives somewhat poor yields of the corresponding secondary alcohols; these occur as optically active forms (Neuberg and Nord, Ber. 1919, 52, 2237, 2248).

(3) Ketones resist the action of oxidising agents to a far greater extent than aldehydes. They do not readily reduce ammoniacal silver solutions; the resistency to alkaline oxidation is instanced by the fact that substances may be dissolved in acetone for treatment with permanganate. Ketones are, however, attacked by chromic acid, the carboxyl group usually remaining attached to the smaller hydrocarbon radicle; thus methyl propyl ketone yields a mixture of acetic and propionic acids, but a good deal depends on the nature of the radicle (Popow, Annalen, 1872, 161, 285). Wagner has found that propyl *iso*butyl ketone gives propionic and *iso*valeric acids, whilst, when ethyl *iso*propyl ketone is oxidised, for every molecule of acetic and *iso*butyric acids produced, 4 molecules of acetone and propionic acid are formed (Ber. 1882, 15, 1194; 1885, 18, 2266; J. Russ. Phys. Chem. Soc. 1884, 16, 645).

Oxygen may also be added to ketones without rupturing the molecule; thus by the use of Caro s acid, acetone gives a peroxide $C_3H_6O_2$ (A. v Baeyer and V. Villiger, Ber. 1899, 32, 3627; 1900, 33, 124, 859; *see* also J. Pastureau, Bull. Soc. chim. 1909, [iv.] 5, 227).

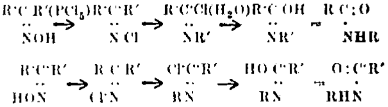
(4) Ketones react less readily than aldehydes with ammonia. Moureu and Mignonac have published a collected account of their work on ketimines (Ann. chim. 1920, [ix.] 14, 322). Keto-anils are obtained by the action of aromatic amines on aliphatic ketones in the presence of iodine (E. Knoevenagel, Ber. 1921, 54, 1722).

Ketones resemble aldehydes in giving oximes, although not always as easily as aldehydes

$$(CH_3)_2C:O+H_2NOH=H_2O+(CH_3)_2C:NOH$$

(V. Meyer, and Janny Ber. 1882, 15, 1324; Janny, *ibid.* 1778; *cf.* Lapworth and Steele, Chem. Soc. Trans. 1911, 1884; Clarke, Lapworth and Wechsler, *ibid.* 1908, 30).

When the radicles connected with the carbonyl group are different, two oximes may be produced from a monoketone. The isomerism in such cases is generally referred to different spatial arrangement (Hantzsch and Werner, Ber. 1890, 23, 11). In determining the configuration of stereoisomeric oximes considerable use has been made of the Beckmann rearrangement (Ber. 1886, 19, 992), whereby they may be converted into one of two structurally isomeric substituted acid amides :

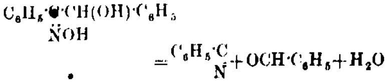


$$\underset{NOH}{R{\cdot}C{\cdot}R'} \xrightarrow{(PCl_5)} \underset{NCl}{R{\cdot}C{\cdot}R'} \rightarrow \underset{NR'}{R{\cdot}C{\cdot}Cl} \xrightarrow{(H_2O)} \underset{NR'}{R{\cdot}C{\cdot}OH} \rightleftharpoons \underset{NHR}{R{\cdot}C{:}O}$$

$$\underset{HON}{R{\cdot}C{\cdot}R'} \rightarrow \underset{ClN}{R{\cdot}C{\cdot}R'} \rightarrow \underset{RN}{Cl{\cdot}C{\cdot}R'} \rightarrow \underset{RN}{HO{\cdot}C{\cdot}R'} \rightleftharpoons \underset{RHN}{O{:}C{\cdot}R'}$$

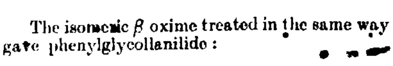
In effecting the transformation, a very dilute and strongly cooled ethereal solution of the oxime is treated with a considerable excess of phosphorus pentachloride, which is added in small portions at a time. The ethereal solution is decanted from the excess of the pentachloride and shaken with ice-cold water, separated and dried by potassium carbonate. The substituted amide is left on evaporation.

The rearrangement may sometimes be effected by warming for 1 hour with 10 parts of sulphuric acid on the water bath, whilst benzene-sulphonyl chloride has been used by Tiemann and Pinnow (Ber. 1891, 24, 4162) and A. Werner and A. Pignet (Ber. 1904, 37, 4295). The latter chemists determined the configuration of the oximes of benzoïn in the following manner: 5 grams of α-benzoïn oxime were dissolved in 20 c.c. of pyridine, 4 grams of benzene-sulphonyl chloride added drop by drop, and the mixture allowed to stand 3 hours at the ordinary temperature. After adding dilute sulphuric acid, the benzaldehyde and benzonitrile were extracted with ether :



$$\underset{NOH}{C_6H_5{\cdot}C{\cdot}CH(OH){\cdot}C_6H_5} = \underset{N}{C_6H_5{\cdot}C}+OCH{\cdot}C_6H_5+H_2O$$

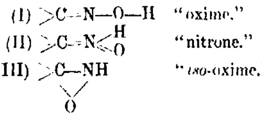
The isomeric β oxime treated in the same way gave phenylglycollanilide :



$$\underset{HON}{C_6H_5{\cdot}C{\cdot}CH(OH){\cdot}C_6H_5} \rightarrow \underset{C_6H_5{\cdot}HN}{O:C{\cdot}CH(OH){\cdot}C_6H_5}$$

Doubt has been cast on the stereochemical interpretation of the isomerism of the oximes. The structural identity of *syn-* and *anti*-benzaldoximes (Goldschmidt, Ber. 1889, 22, 3113) is difficult to reconcile with the fact that both compounds give the same derivative with phenylcarbimide (Brady and Dunn, Trans. Chem. Soc.). Atack (Trans. Chem. Soc.

1921, 119, 1175) supposes that oximes may correspond to the three constitutions:


$$\text{(I)}\ >C=N-O-H\quad\text{"oxime."}$$
$$\text{(II)}\ >C=N\!<\!\genfrac{}{}{0pt}{}{H}{O}\quad\text{"nitrone."}$$
$$\text{(III)}\ >C-NH\ (\text{ring through } O)\quad\text{"}\textit{iso}\text{-oxime."}$$

Substances of type (II) would be difficult to isolate, but alkyl compounds would be more stable and the N-phenyl ether of benzophenone oxime, $(C_6H_5)_2C:N\!<\!\genfrac{}{}{0pt}{}{C_6H_5}{O}$, has been described by Staudinger and Miescher (Helv. Chim. Acta, 1919, 2, 562). It is of interest that the direct methylation of benzophenone oxime gives N— and O— methyl ethers (Semper and Lichtenstadt, Ber. 1918, 51, 933; see also Alessandri, Gazzetta, 1921, 51, i. 75.

(5) Ketones containing the group $\cdot CO\cdot CH_2\cdot$ react with nitrous acid, giving the monoximes of diketones:

$$CH_3\cdot CO\cdot CH_2\cdot CH_3+HNO_2 = CH_3\cdot CO\cdot C(:NOH)\cdot CH_3+H_2O$$

(L. Claissen and Manasse, Ber. 1889, 22, 526; O. Diels, Ber. 1902, 35, 3290; 1907, 40, 4336).

(6) Ketones react with hydrazine to give ketazines (Curtius and Thun, J. pr. Chem. 1891, [ii.] 44, 161):

$$2R\cdot CO\cdot R'+N_2H_4=2H_2O+RR'C:N\cdot N:CRR'$$

or hydrazones (E. Fischer, Annalen, 1878, 190, 136; Ber. 1883, 16, 661, 2241; 1884, 17, 572; 1889, 22, 90; 1897, 30, 1240):

$$R\cdot CO\cdot R'+H_2N\cdot NHR''=H_2O+RR'C:N\cdot NH\cdot R$$

In using phenylhydrazine, a dilute acetic acid solution is generally employed; where hydrazone formation only takes place with difficulty the ketone may be dissolved in glacial acetic acid, treated with a slight excess of phenylhydrazine and allowed to stand in the cold. In certain cases (*e.g.* carvole, v. Baeyer, Ber. 1894, 27, 813) the ketone and phenylhydrazine may be mixed in equimolecular proportions without solvent and allowed to stand.

In many cases the use of phenylhydrazine for the isolation and identification of aldehydes and ketones may be advantageously replaced by one of the following hydrazino compounds:

p-Bromophenylhydrazine (E. Fischer, Ber. 1891, 24, 4221; L. Michaelis, *ibid.* 1893, 26, 2190).

p-Nitrophenylhydrazine (A. Purgotti, Atti R. Accad. Linc. 1892, 7, ii. 266; E. Bamberger and H. Sternitzki, Ber. 1893, 26, 1306; E. Hyde, *ibid.* 1899, 32, 1810; H. D. Dakin, J. Biol. Chem. 1908, 4, 235).

as-Methylphenylhydrazine $C_6H_5(CH_3)N\cdot NH_2$ (C. Neuberg, Ber. 1902, 35, 959, 2626).

Semicarbazide $NH_2\cdot CO\cdot NH\cdot NH_2$ (Baeyer, Ber. 1894, 27, 1918). With unsaturated ketones of type $C_6H_5\cdot CO\cdot CH:CH\cdot R$, semicarbazido-semicarbazones are formed (Von Auwers, Ber. 1921, 54, 987).

Aminoguanidine $NH_2\cdot C(:NH)NH\cdot NH_2$. The condensation products with ketones may be isolated as well-crystallised picrates (Baeyer, Ber. 1894, 27, 1919).

Thiosemicarbazide $NH_2\cdot CS\cdot NH\cdot NH_2$. The resulting thiosemicarbazones

$$NH_2\cdot CS\cdot NH\cdot N:CRR'$$

give insoluble or sparingly soluble salts of the heavy metals (C. Neuberg and W. Neimann, Ber. 1902, 35, 2049).

Benzhydrazide $C_6H_5\cdot CO\cdot NH\cdot NH_2$ and its *o*-, *m*-, and *p*-nitro- derivatives

$$C_6H_4(NO_2)CO\cdot NH\cdot NH_2$$

With aromatic ketones it is advisable to warm in alcoholic solution; aldehydes react more readily (Curtius and co-workers, J. pr. Chem. 1894, [ii.] 50, 275, 295; 1895, 51, 165, 353).

Dichloroketones do not necessarily react with semicarbazide to give monosemicarbazones. Thus whilst dichloromethyl ethyl ketone reacts normally to give a monosemicarbazone

$$CHCl_2\cdot C(:N\cdot NH\cdot CO\cdot NH_2)\cdot CH_2\cdot CH_3$$

the isomeric methyl dichloroethyl ketone gives the disemicarbazone of diacetyl

$$CH_3\cdot C(:N\cdot CH_3ON_2)\cdot C(:N\cdot CH_3ON_2)\cdot CH_3$$

(Blaise, Compt. rend. 1913, 156, 1549).

References to earlier work on the action of hydrazines on *a*-chloroketones are given by Bodforss, Ber. 1919, 52, 1762.

(7) Ketones react with phosphorus pentachloride as follows:—

$$R\cdot CO\cdot R'+PCl_5=POCl_3+R\cdot CCl_2\cdot R'$$

Sometimes chlorination of one of the radicles R,R′ occurs (Favorski, J. Russ. Phys. Chem. Soc. 1912, 44, 1339).

(8) Some ketones, usually those containing the group $CH_3\cdot CO\cdot$, unite with acid sodium sulphite; acetone, for example, gives

$$(CH_3)_2C(OH)(SO_3Na),H_2O$$

The ketone is regenerated by sodium carbonate solution.

(9) Hydrogen cyanide yields nitriles

$$RR'C(OH)CN$$

which react with ammonia to give the nitriles of *a*-amino acids $RR'C(NH_2)CN$.

A convenient way of preparing *a*-aminonitriles is to dissolve a ketone (or aldehyde) in glacial acetic acid and leave this with a concentrated aqueous solution of potassium cyanide (Von Walther and Hübner, J. pr. Chem. 1916, [ii.] 93, 119).

Aromatic isonitriles react with ketones in presence of acetic acid yielding products of the type $CH_3\cdot CO\cdot O\cdot C(R'R'')\cdot CONHR$ (Passerini, Gazzetta, 1921, 51, ii. 126, 181).

Many ketones react with ethyl cyanoacetate in presence of ammonia to form piperidones, *e.g.* benzyl methyl ketone yields 3:5-dicyano-2:6-diketo-4-benzyl-4-methylpiperidone (Guareschi, Gazzetta, 1918, 48, ii. 83. Compare J. F. Thorpe, Trans. Chem. Soc. 1911, 99, 1424, and Kon and Thorpe, Trans. Chem. Soc. 1919, 115, 686).

(10) Hydrogen sulphide converts the ketones into thioketones, *e.g.* acetone yields thioacetone (W. Spring, Bull. Acad. Roy. Belg. 1883, [iii.] 5, 236).

(11) The ketones do not so readily form addition products as the aldehydes, *e.g.* with water and alcohol, but when a mixture of a ketone and a mercaptan is treated with gaseous

hydrogen chloride a marcaptol is formed (Baumann, Ber. 1885, 18, 887):

$$(CH_3)_2CO+2C_2H_5SH=H_2O+CH_3)_2C(SC_2H_5)_2$$

(12) Polyhalogenated ketones and polyketones are exceptional, thus trichloracetone gives a hydrate $CCl_3{\cdot}C(OH)_2{\cdot}CH_3$.

(13) The acetals of the ketones (as well as of the aldehydes) may be obtained by the action of orthoformic esters (Claisen, Ber. 1907, 40, 3903):

$$RR'C:O+HC(OC_2H_5)_3 = RR'C(OC_2H_5)_2+H{\cdot}CO{\cdot}OC_2H_5$$

The ketone and calculated amount of ethyl formate are dissolved in alcohol (3 or more molecular proportions) and a small amount of mineral acid, ferric chloride, &c., as catalysing agent added. The mixture is either warmed for a short time or allowed to stand for a longer period at the ordinary temperature.

Nascent ethyl orthoformate from alcohol and ethyl iminoformate hydrochloride may also be used (*cp.* E. Hess, D. R. P. 197804):

$$H{\cdot}C(:NH,HCl)(OC_2H_5)+2C_2H_5OH = NH_4Cl+H{\cdot}C(OC_2H_5)_3$$

(*see* Pinner, Ber. 1883, 16, 356).

(14) Many ketones, notably cyclic ketones, behave towards acylating agents as if they possessed the tautomeric enolic structure, thus *cyclo*hexanone gives esters of *cyclo*hexenol (C. Mannich, Ber. 1906, 39, 1594; 1908, 41, 564; *cp.* F. W. Semmler, *ibid.* 1909, 42, 584, 1161, 2014). A striking example is the conversion of diethyl and dipropyl ketones into acetyl derivatives of their enolic forms by heating with 11 parts of acetic anhydride, and ½ part of fused sodium acetate for 70 hours at 205°–215° (V. Hâncu, Ber. 1909, 42, 1052). Keto-enol tautomerism is discussed more fully in connection with ethyl acetoacetate.

(15) Magnesium alkyl halides react with ketones, giving tertiary alcohols:

$$C_6H_5{\cdot}CO{\cdot}CH_3+CH_3{\cdot}MgI=C_6H_5{\cdot}C(OMgI)(CH_3)_2$$

$$C_6H_5{\cdot}C(OMgI)(CH_3)_2+H_2O = Mg(OH)I+C_6H_5{\cdot}C(CH_3)_2(OH)$$

(V. Grignard, Compt. rend. 1900, 130, 1322; Bull. Soc. chim. 1901, [iii.] 25, 497; Ann. Univ. Lyon. 1901, No. 6, 1-116).

(16) A mixture of alkyl halide and sodium frequently behaves like the Grignard reagents. P. Schorigin has obtained diphenyl ethyl carbinol $C(C_6H_5)_2(C_2H_5)OH$ by the action of 21·5 grams of sodium wire on 30 grams each of ethyl iodide and benzophenone dissolved in 150 c.c. of dry benzene (Ber. 1908, 41, 2711).

(17) Ketones containing at least one aliphatic radicle react with esters and sodium ethoxide to give *β*-diketones. In this way benzoylacetone may be obtained from ethyl benzoate and acetone (Claisen, Ber 1887, 20, 655), or from ethyl acetate and acetophenone (Beyer and Claisen, *ibid.* 2180; *see* also R. W. L. Clarke, A. Lapworth, and E. Wechsler, Chem. Soc. Trans. 1908, 93, 30).

(18) Ketones of suitable structure react with 1 or 2 molecules of an aldehyde giving unsaturated ketones. Methyl styryl ketone (monobenzalacetone) may be prepared by adding 10 parts of 10 p.c. caustic soda solution to a mixture of 10 parts of benzaldehyde, 900 parts of water, and 20 parts of acetone, allowing to stand 2 or 3 days in the cold, extracting with ether and distilling under reduced pressure:

$$C_6H_5{\cdot}CHO+CH_3{\cdot}CO{\cdot}CH_3 = H_2O+C_6H_5{\cdot}CH:CH{\cdot}CO{\cdot}CH_3$$

Benzalacetone forms shining tabular crystals, m.p. 41°–42°, b.p. 260°–262°, b.p. (at 25 mm.) 151°–153° (Claisen and Ponder, Annalen, 1884, 223, 139; Langlois, Compt. rend. 1919, 168, 1052).

On reducing the ethylenic linkage by hydrogen in presence of platinum black, *α*-phenylbutane-*γ*-one, b.p. 110°–112°/12 mm., is produced. Further reduction gives *α*-phenylbutane-*γ*-ol and *α*-cyclohexylbutane-*γ*-ol (Vavon, Compt. rend. 1912, 154, 1705).

Substitution derivatives, *e.g.* *o*-hydroxystyryl methyl ketone, are of interest (Harries, Ber. 1891, 24, 3180; Decker and Feher, Ber. 1908, 41, 2997; Heilbron and Buck, Trans. Chem. Soc. 1921, 119, 1503).

If, however, to 20 parts of benzaldehyde, 6 parts of acetone and 40 parts of acetic acid, 30 parts of sulphuric acid are added drop by drop whilst the mixture is cooled very thoroughly, dibenzalacetone is formed. The mixture, after standing 6–8 hours at 0°, is poured into water, the precipitate washed with caustic soda and crystallised from ether. Monoclinic crystals, m.p. 112°–112·5°.

$$2C_6H_5{\cdot}CHO+CH_3{\cdot}CO{\cdot}CH_3 = 2H_2O+C_6H_5{\cdot}CH:CH{\cdot}CO{\cdot}CH:CH{\cdot}C_6H_5$$

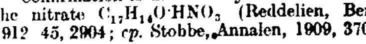
(Claisen and Claparède, Ber. 1881, 14, 2460).

Reduction of distyryl ketone by Paal's method gives di-*β*-phenylethyl ketone, b.p. 224°/18 mm. (Borsche, Ber. 1912, 45, 46). Into the latter compound, four methyl groups can be introduced by means of sodamide and methyl iodide (Haller, Compt. rend. 1912, 154, 555). The reaction with phosphorus pentachloride is abnormal (Annalen, 1912, 393, 235).

pp′-Tetramethyldiaminodistyryl ketone (Sachs and Lewin, Ber. 1902, 35, 3576) lacks reactivity towards *β*-diketones and *β*-ketonic esters in presence of piperidine (Borsche, Annalen, 1910, 375, 145). On the other hand, 4′-dimethylamino-2-hydroxydistyryl ketone (m.p. 154° decomp.) is a very reactive compound which forms a number of coloured addition products (Heilbron and Buck, Trans. Chem. Soc. 1921, 119, 1500).

p-Amino and *p*-acetamino-acetophenone may be condensed with aldehydes (Giua and Bagiella, Gazzetta, 1921, 51, ii. 116).

The coloration produced by strong acids with dibenzalacetone is attributed by Baeyer and Villiger to the formation of quinonoïd carbonium salts (Ber. 1902, 35, 1189, 3013), *e.g.*:



$$\frac{H}{Cl}\!>\!C_6H_4\!=\!CH{\cdot}CH:C(OH)CH:CH{\cdot}C_6H_5$$

Confirmation is afforded by the isolation of the nitrate $C_{17}H_{14}O{\cdot}HNO_3$ (Reddelien, Ber. 1912 45, 2904; *cp.* Stobbe, Annalen, 1909, 370, 90 *et seq.*).

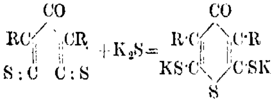
Acetophenone can only react with one molecule of benzaldehyde giving phenyl styryl ketone (chalkone). Hydroxy-derivatives of phenyl styryl ketone occur in nature.

Numerous derivatives of chalkone have been prepared. The original method of preparing phenyl styryl ketone (Claisen, Ber. 1887, 20, 665) has been improved by Abell (Chem. Soc.

Trans. 1912, 101, 1000), who adds 12 c.c. of 20 p.c. solution of sodium methoxide in methyl alcohol to a mixture of 48 grams of benzaldehyde and 48 grams of acetophenone.

(19) Ketones react with carbon disulphide in presence of caustic alkalis, giving 4-keto-3 : 5-dialphylpenthiophen-2 : 6-dithiols :

$$R{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}R+2CS_2+4KOH$$
$$=SC:CR{\cdot}CO{\cdot}CR:C:S+4H_2O+2K_2S$$



(H. Apitzsch, Ber. 1904, 37, 1599; 1905, 38, 2888; 1908, 41, 4028, 4039, 4047; 1909, 42, 2940; 1910, 43, 1259).

(20) At 180°–200° hydrogen (with nickelised asbestos as catalytic agent) reduces unsaturated to saturated ketones (G. Darzens, Fr. Pat. 350390).

Differentiation of Ketones from Aldehydes.

Aldehydes and ketones possess many reactions in common, but, on oxidation, the ketones do not give acids containing the same number of carbon atoms as the ketone (General Reaction 3).

A. Einhorn finds that aldehydes react with catechol monocarbazinic ester

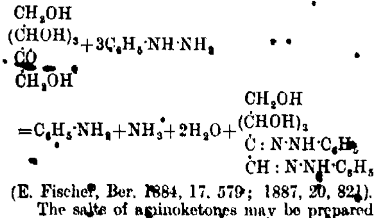
$$C_6H_4(OH)O{\cdot}CO{\cdot}NH{\cdot}NH_2$$

in dilute alcoholic solution, whilst ketones do not, although condensation may be effected in a few cases when glacial acetic acid or zinc chloride is employed as condensing agent (Annalen, 1898, 300, 135; 1901, 317, 190). Resorcinol and quinol monocarbazinates behave similarly.

A. Angeli finds that nitrohydroxylamine and other 'nitroxyl' (NOH) yielding substances convert aldehydes directly into the corresponding hydroxamic acids (Gazz. chim. ital. 1904, 34, i. 50).

Hydroxyl and Amino Substituted Ketones.

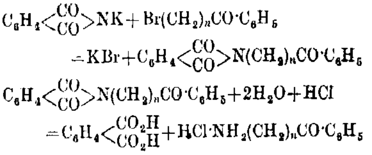
The substituted ketones usually exhibit the specific ketonic characters as well as properties due to the substituent groups. Thus keto alcohols form esters, and amino ketones are basic. The different groupings may, however, affect one another, keto alcohols of the type $R{\cdot}CO{\cdot}CH_2OH$ usually give osazones, as lævulose when warmed with phenylhydrazine solutions gives phenylglucosazone :



$$\begin{array}{l}CH_2OH\\ \dot{C}HOH)_3\\ \dot{C}O\\ \dot{C}H_2OH\end{array}+3C_6H_5{\cdot}NH{\cdot}NH_2$$
$$=C_6H_5{\cdot}NH_2+NH_3+2H_2O+\begin{array}{l}CH_2OH\\ (\dot{C}HOH)_3\\ \dot{C}:N{\cdot}NH{\cdot}C_6H_5\\ \dot{C}H:N{\cdot}NH{\cdot}C_6H_5\end{array}$$

(E. Fischer, Ber. 1884, 17, 579; 1887, 20, 821).

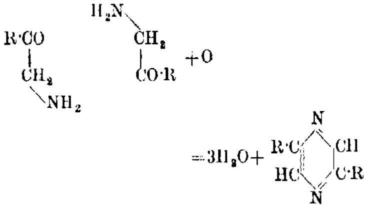
The salts of aminoketones may be prepared from the halogenised ketones by condensation with potassium phthalimide and subsequent hydrolysis (Gabriel, Ber. 1907, 40, 2649; 1908, 41, 242, 513, 1127, 2010, 2014; 1909, 42 1238, 1249, 1259; 1910, 43, 356; 1911, 44, 57, 3090; 1914, 47, 1336).



$$C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{CO}{>}NK+Br(CH_2)_nCO{\cdot}C_6H_5$$
$$=KBr+C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{CO}{>}N(CH_2)_nCO{\cdot}C_6H_5$$
$$C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{CO}{>}N(CH_2)_nCO{\cdot}C_6H_5+2H_2O+HCl$$
$$=C_6H_4{<}\genfrac{}{}{0pt}{}{CO_2H}{CO_2H}+HCl{\cdot}NH_2(CH_2)_nCO{\cdot}C_6H_5$$

Other recent papers on amino-ketones: Forster, Chem. Soc. Trans. 1911, 99, 239; Mannich, Ber. 1911, 44, 1542; André, Compt. rend. 1912, 155, 52; Böttcher, Ber. 1913, 46, 3158; Haller and Ramart-Lucas, Ann. Chim. 1917, [ix.] 8, 5; Hale and Britton, J. Amer. Chem. Soc., 1919, 41, 841, 1020; McKenzie and Barrow, Trans. Chem. Soc. 1921, 119, 69).

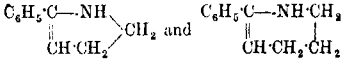
a-Aminoketones, when isolated from their salts, condense in the following manner :



β-Aminoketones are capable of existence as free bases, *e.g.* diacetoneamino

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}C(CH_3)_2NH_2$$

γ- and *δ*-aminoketones condense internally, giving substituted pyrrolines and tetrahydropyridines respectively, *e.g.* :



ε-Aminoketones are stable.

INDIVIDUAL OPEN-CHAIN MONOKETONES.

1. *Aliphatic Ketones.*

Acetone is treated in a separate article (*q.v.*). It forms basic products with ammonia, diacetoneamine $CH_3{\cdot}CO{\cdot}CH_2{\cdot}C(CH_3)_2NH_2$ (Heintz, Annalen, 1877, 189, 214; Everest, Trans. Chem. Soc. 1919, 115, 588; Patterson and McMillan, Trans. Chem. Soc. 1921, 119, 269) and triacetoneamine $NH{<}\genfrac{}{}{0pt}{}{C(CH_3)_2CH_2}{C(CH_3)_2CH_2}{>}CO+H_2O$ Heintz, *ibid.* 1875, 178, 305), the former of which has found application in the preparation of pharmaceutical products (Schering, D. R. PP. 95620, 95621, 95622, 95623; *cp.* Harries, D. R. PP. 99004, 99005).

The hypnotic, 'sulphonal'

$$(CH_3)_2C(SO_2C_2H_5)_2$$

is obtained either by the oxidation of the mercaptol $(CH_3)_2C(SC_2H_5)_2$ with potassium permanganate (Baumann, Ber. 1886, 19, 2808), or by the methylation of ethylidene diethylsulphone $CH_3{\cdot}CH(SO_2C_2H_5)_2$, or diethylsulphonemethane $CH_2(SO_2C_2H_5)_2$ with alcoholic potash and methyl iodide (Fromm, Annalen, 1889, 253, 147) (*v.* SULPHONAL).

The halogen derivatives of acetone affect the eyes and nose painfully. The chloro-acetones and other chlorinated ketones have recently received considerable attention (Lippmann, Ber. 1912, 45, 2489; Blaise, Compt. rend. 1912, 155, 46; 1913, 156, 793; Bull. Soc. chim. 1914, [iv.] 15, 728; 1915, [iv.] 17, 425; Wohlgemuth, Ann. Chim. 1914, [ix.] 2, 403).

In preparing monobromoacetone and other monobromoketones, J. D. Riedel adds a solution of bromine in bromide liquor to a hot solution of acetone (or other bromoketone) containing bromoacetone (or bromoketone) in bromide liquor (D.R.PP. 208944, 298353). Thiocyanoacetone (Hellon and Tscherniac, Ber. 1883, 16, 349; Tscherniac, Ber. 1892, 25, 2623; Trans. Chem. Soc. 1919, 115, 1071) yields 2-chloro-4-methylthiazole when treated with hydrogen chloride.

Methyl ethyl ketone (*Butanone*), b.p. 78.6°, sp.gr. 0·8101/15°/4° (Marshall, Chem. Soc. Trans. 1906, 89, 1376), occurs in the distillate from crude calcium acetate, and may be obtained from the water used in washing wool; this is evaporated with lime, and the resultant calcium salts distilled. About 45–50 p.c. of 'acetone oil' is obtained, 80 p.c. is soluble in water, and when fractionated 60 p.c. of methyl ethyl ketone is obtained. This compound is employed for the denaturation of alcohol, the similarity of boiling-points making separation by fractionation nearly impossible (A. and P. Buisine, Compt. rend. 1897, 125, 777; 1898, 126, 231; 1899, 128, 561) (*v.* ACETONE OIL). For production from *n*-Butyl alcohol, *see* King, Chem. Soc. Trans. 1919, 115, 1404. Vapour pressure of mixtures with acetone (T. W. Price, *ibid.* 1116).

Methyl ethyl ketone condenses with ethyl formate in presence of sodium ethoxide to give hydroxymethylene-butanone

$$CH_3{\cdot}CO{\cdot}C(:CHOH){\cdot}CH_3$$

The latter compound is also obtained from azibutanone $CH_3{\cdot}CO{\cdot}C(N_2){\cdot}CH_3$ and formaldehyde (Diels and Ilberg, Ber. 1916, 49, 158). Other derivatives, *see* Sen-Gupta, Chem. Soc. Trans. 1914, 105, 403.

Isoprene can be obtained by condensing methyl ethyl ketone with diethylamino-methyl alcohol, reducing the diethyl-γ-keto-β-methylbutylamine so found to a hydroxy compound, forming a quarternary ammonium compound from the latter, and finally treating with alkali (Fr. Bayer & Co., D. R. P. 267040; *cf.* D. R. PP. 254714, 266656, 267347). Condensations of methyl ethyl ketone with a number of aldehydes are described by Ryan and Devine (Proc. R. Irish Acad. 1916, 32, B, 208). A diketone $CH_3{\cdot}CO{\cdot}CH(CH_3){\cdot}CH(CH_3){\cdot}CO{\cdot}CH_3$ is produced on exposing methyl ethyl ketone to light (Ciamician and Silber, Ber. 1912, 45, 1540).

Methyl ethyl ketone, like acetone, may be employed instead of formaldehyde for preparing sulphoxylates (M. L. B., D. R. PP. 162875, 207846, 210467).

Methyl hydroxyethyl ketone

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}OH$$

results from the condensation of acetone and formaldehyde; dehydrated by means of 2 p.c. of zinc chloride *methyl vinyl ketone*

$$CH_3{\cdot}CO{\cdot}CH:CH_2$$

b.p. 80°, is formed (Farbenfab. vorm. Fr. Bayer & Co., D. R. PP. 222551, 223207, 242612).

Methyl propyl ketone (2-pentanone) is found in the crude acetone obtained by distilling the calcium salts from pyroligneous acid, b.p. 101·7°.

Methyl-*n*-amyl ketone (2-heptanone) occurs in oil of cloves (Schimmel & Co., Ber. April, 1897, 50) and boils at 151°–152°. It possesses a penetrating fruity odour.

Methyl nonyl ketone (2-undecanone) forms the chief constituent of oil of rue (*Ruta graveolens* [Linn.]), being accompanied by a small amount of a ketone $C_{12}H_{24}O$ (Williams, Annalen, 1858, 107, 374). It also forms 75 p.c. of the ketonic portion of the 'essence' of cocoa-nut butter, in which it is accompanied by methyl heptyl and methyl undecyl ketones (A. Haller and A. Lassieur, Compt. rend. 1910, 151, 697).

Methyl nonyl ketone also occurs in palm-kernel oil (Salway, Chem. Soc. Trans. 1917, 111, 407).

2-Methyl-Δ²-heptene-6-one

$$(CH_3)_2C:CH{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_3$$

occurs in oil of linaloes (Barbier and Bouveault, Compt. rend. 1895, 121, 168), and is a constituent of lemon-grass oil (Bertram and Tiemann, Ber. 1899, 32, 834), b.p. 173°–174°, sp.gr. 0·8602, at 20° n_D^{20} 1·4445. This ketone has been artificially prepared by the slow distillation of cineolic anhydride $C_{10}H_{14}O_4 = C_8H_{14}O + CO + CO_2$ (Wallach, Annalen, 1890, 258, 324), and together with other substances by the oxidation of geraniol, geranial, and methylheptenol by chromic acid (Tiemann and Semmler, Ber. 1893, 26, 2722). The same authors also obtained it by boiling geranonitrile with alcoholic potash and by the oxidation of citral (Ber. 1895, 28, 2126).

Verley (Bull. Soc. chim. 1897, [iii.] 17, 175) obtains it by boiling 500 grams of citral with a solution of 500 grams of potassium carbonate in 5 litres of water for 12 hours, the ketone is then distilled in steam and fractionated under reduced pressure. Verley records the constants, b.p. 168° (84° at 26 mm.), sp.gr. 0·910 at 14°, $n_D^{31°}$ 1·437.

Methylheptenone gives an *oxime* and *phenylhydrazone*; it is converted into dihydro-*m*-xylene by the action of zinc chloride (Wallach) or concentrated sulphuric acid (Verley); whilst on reduction electrolytically, methylheptenol is produced (Law, Chem. Soc. Trans. 1912, 101, 1022).

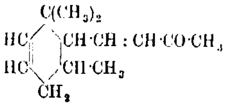
Zibethone $C_{17}H_{30}O$, m.p. 32·5°, b.p. 206°–208°/17 mm., occurs in civet. *Oxime*, m.p. 92°; *semicarbazone*, m.p. 187° (Erwin Sack, D. R. P. 279313).

II. *Hydroaromatic Ketones.*

Of the non-cyclic ketones containing hydroaromatic nuclei, irone, and its isomers are of especial importance.

Irone $C_{13}H_{20}O$ was recognised by Tiemann and Krüger (Ber. 1893, 26, 2675; 1895, 28, 1754; Tiemann, *ibid.* 1898, 31, 808; Haarmann and Reimer, D. R. P. 72840) as the odoriferous principle of iris root (*Iris florentina* [Linn.], *I. germanica* [Linn.], *I. pallida* [Linn.]). Violet or iris oil is obtained chiefly from *I. florentina*; at ordinary temperatures it forms a fairly firm yellowish mass, possessing an intense odour of violets. It consists of about 80 p.c. of myristic acid associated with irone, methyl myristate, oleic aldehyde, acid, and esters. Irone and volatile esters distil in a current of steam, the esters are saponified, the irone again steam distilled, and the product rectified under reduced pressure. Pure irone is dextrorotatory, b.p. (16 mm.) 144°, sp.gr. at 20° 0·939; *oxime* $C_{13}H_{20}:NOH$, m.p. 121·5°; *p*-bromo-phenylhydrazone $C_{13}H_{20}:N·NH·C_6H_4Br$, m.p. 140°-145°.

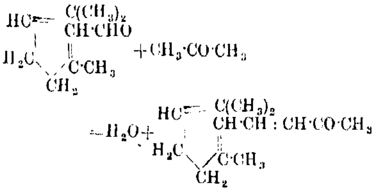
Tiemann and Kruger (*l.c.*) determined the constitution of irone as



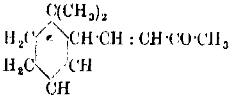
and attempted to synthesise it from citral (lemon-grass oil).

Ionones (*a*- and *β*). These ketones, isomeric with irone, and differing from it and from one another by the position of the double linkage in the ring, were actually obtained from citral; as they also have an odour of violets they have attained very considerable technical importance (Haarmann and Reimer, D. R. PP. 73089, 75128).

Citral and acetone are condensed to *ψ*-ionone:

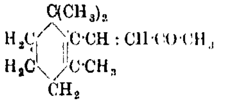


which, on boiling with sulphuric acid, gives a mixture of



a-Ionone

and



β-Ionone

The formation of the former is favoured by a dilute acid, the latter when more concentrated sulphuric acid is employed. The separation of the two isomerides is effected by the more sparing solubility of the bisulphite compound of *a*-ionone (Tiemann, Ber. 1898, 31, 870), the process may be aided by salting out with sodium chloride (Chuit, Rev. gén. Chim. pure appl. 1903, 6, 422).

According to patent D. R. P. 120027 *a*-ionone is formed preferentially with concentrated phosphoric acid at 30°, *β*-ionone almost exclusively when 70–100 p.c. sulphuric acid is employed in the cold (Haarmann and Reimer).

Citral may be isomerised to *a*- and *β*-*cyclo*-citrals, which condense with acetone, yielding ionones (Haarmann and Reimer, D. R. P. 123747; Tiemann, Ber. 1900, 33, 3721). Other information about the preparation of ionones and higher homologues using methyl ethyl and methyl *iso*propyl ketones in place of acetone is given in Haarmann and Reimer's patents (D. R. PP. 126959, 126960, 127424, 127831, 129027, 132222, 133758, 150827, 183855).

a-*Ionone* is an oil with strong, sweet smell of fresh violets, b.p. (12 mm.) 127·6°, sp.gr. at 20° 0·9301; *oxime* $C_{13}H_{20}:NOH$, m.p. 89°–90°; *semicarbazone* $C_{13}H_{20}:N·NH·CO·NH_2$, m.p. 107°-108°.

β-*Ionone* is also an oil smelling pleasantly like violets, b.p. (10 mm.) 127°-128·5°; sp.gr. at 20° 0·9442; *oxime*, oily; *semicarbazone*, m.p. 148°-149°. Four hydrogen atoms may be added to *a*- and *β*-ionones or to irone in presence of colloidal palladium or platinum black (Ruzicka, Helv. Chim. Acta, 1919, 2, 352).

A ketone $C_9H_{14}O$, isolated from the Indian deodar (*Cidrus deodara*), is probably a *p*-methyl-tetrahydroacetophenone (Roberts, Chem. Soc. Trans. 1916, 109, 793).

III. *Mixed Ketones.*

Acetophenone $C_6H_5·CO·CH_3$, used medicinally as *hypnone*, is formed by distilling a mixture of calcium acetate and benzoate, and is conveniently prepared by the action of acetyl chloride on benzene in the presence of aluminium chloride (Friedel and Crafts, Ann. Chim. 1884, [vi.] 1, 507), m.p. 20·5°, b.p. 202°, sp.gr. 1·032 at 15°.

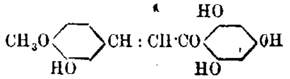
Acetophenone does not combine with sodium bisulphite; phosphorus pentachloride gives $C_6H_5·CCl_2·CH_3$; halogens substitute in the methyl group (Gautier, Bull. Soc. chim. 1886, 45, 875). The *phenylhydrazone* has m.p. 105°.

The methyl group of acetophenone may be alkylated in presence of sodamide (Haller and Bauer, Compt. rend. 1909, 143, 70). When acetophenone is heated with sodium ethoxide to 130°–140°, some 3 : 5-diphenyl-methyl-benzene is formed (Gastaldi and Cherchi, Gazz. chim. ital. 1915, 45, ii. 251; 1920, 50, i. 71).

Acetophenone condenses with benzaldehyde, giving *styryl phenyl ketone*

$$C_6H_5·CH:CH·CO·C_6H_5$$

Derivatives of this compound occur naturally; *e.g.* hesperitin and homoeriodictyol to which are assigned the respective structures:



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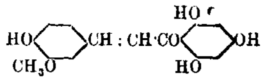


(Power and Tutin, Trans. Chem. Soc. 1907, 91, 887; *cp.* Tiemann and Will, Ber. 1881, 14, 970; Perkin, Chem. Soc. Trans. 1898, 73, 1037; and Tutin and Caton, *ibid.* 1910, 97, 2062). Butein is 2 : 4-dihydroxyphenyl-3 : 4-dihydroxystyryl ketone, its synthesis was effected by Göschke and Tambor (Ber. 1911, 44, 3502; 1912, 45, 186).

ω-**Chloroacetophenone** (phenacyl chloride) $C_6H_5·CO·CH_2Cl$ is obtained by leading the theoretical amount of chlorine into boiling acetophenone. The product is distilled, the portion passing over below 200° is chlorinated again, whilst the fraction between 240° and 250° is collected separately, and the monochloro-derivative crystallised by cooling; m.p. 58°–59°; b.p. 244°–245° (Staedel, Ber. 1887, 10, 1830).

ω-**Bromoacetophenone** $C_6H_5{\cdot}CO{\cdot}CH_2Br$ is prepared by adding gradually one molecular proportion of bromine to acetophenone dissolved in carbon disulphide (Hunnius, Ber. 1877, 10, 2007), a current of dry carbon dioxide being led through (Staedel, Kleinschmidt, *ibid.* 1880, 13, 837; 1883, 16, 22); m.p. 50°.

Both phenacyl chloride and bromide are of use as synthetic agents; thus with ammonia 2:5-diphenylpyrazine is produced (Gabriel, Ber. 1908, 41, 1127; Tutin, Chem. Soc. Trans. 1910, 97, 2495) a compound previously described by Staedel and Rugheimer as isoindol (Ber. 1876, 9, 563; 1880, 13, 836). Phenacyl sulphide is of interest on account of the stereoisomerism of certain derivatives (Fromm and Flaschen, Annalen, 1912, 394, 310).

p-**Aminoacetophenone** $NH_2{\cdot}C_6H_4{\cdot}CO{\cdot}CH_3$, m.p. 106°; b.p. 293°–295°. One method of preparing this compound has been given previously (general methods of preparation, 17). F. Kunckell (Ber. 1900, 33, 2641) obtains *p*-acetylaminoacetophenone by the action of 70 grams of aluminium chloride on a mixture of 20 grams of acetanilide, and 50 grams each of carbon disulphide and acetyl chloride, a yield of 15·5 grams (m.p. 166°–167°) being obtained. The free aminoketone is readily obtained by boiling for half an hour with three times its weight of 15 p.c. hydrochloric acid, and precipitating with sodium carbonate.

The hydrochlorides of *o*- and *p* aminoacetophenone give coloured solutions in alcohol; solutions made from the *m*-isomeride are colourless. This agrees with a quinonoid structure for the two former (Kuhara, Saito and Shimomura, Mem. Coll. Sci. Kyoto, 1920, 4, 201).

o-**Hydroxyacetophenone** $HO{\cdot}C_6H_4{\cdot}COCH_3$ was first obtained by ketonic fission of *o*-methoxybenzoylacetic ester and subsequent splitting off of the methyl group (Tahara, Ber. 1892, 25, 1306). It has been found by Dunstan and Henry in the oil of *Chiona glabra* (Chem. Soc. Trans. 1899, 75, 67), b.p. 213°/717 mm. *Acetyl derivative*, m.p. 89°; *oxime*, m.p. 102°; *phenylhydrazone*, m.p. 108°.

m-**Hydroxyacetophenone**, m.p. 96° (Biginelli, Gazz. chim. ital. 1894, 24, i. 440; Besthorn, Ber. 1894, 27, 3042).

p-**Hydroxyacetophenone** may be obtained from the amino compound by diazotisation; m.p. 107° (Klingel, Ber. 1885, 18, 2691).

Resacetophenone

$$CH_3{\cdot}CO{\cdot}C_6H_3(OH)_2\ (OH:OH=2:4$$

a compound of synthetical importance, is obtained as described in General Method 17; m.p. 142°.

Gallacetophenone $2:3:4\text{-}(OH)_3C_6H_2{\cdot}CO{\cdot}CH_3$ similarly obtained from acetic acid and pyrogallol is used as a mordant dyestuff. The analogous purely aromatic hydroxy ketones, which are similarly employed, are described later.

Various condensations of resorcinol and phloroglucinol with fatty acids have been effected (P. Karrer and S. Rosenfeld. Helv. Chim. Acta, 1921, 4, 707). Acetic acid condenses with the naphthols to hydroxynaphthyl methyl ketone (K. Fries, Ber. 1921, 54, 709).

o-, *m*-, and *p*-Tolyl methyl ketones (b.ps. 211°, 221°, and 224·5° at 745 mm.) and other tolyl alkyl ketones have been prepared by passing the vapours of the corresponding aromatic and fatty acids over thorium oxide at 460°–470° (Senderens, Compt. rend. 1911, 152, 90).

Zingerone $C_{11}H_{14}O_3$ has been isolated from the extract of ginger (*Zingiber officinalis*), m.p. 40°–41° (Nomura, Chem. Soc. Trans. 1917, 111, 769) or 31°–34° (Lapworth, Royle and Pearson, *ibid.* 777). Its constitution is that of 4-hydroxy-3-methoxyphenylethyl methyl ketone. It has been synthesised by condensing vanilline with acetone, and subsequently reducing (Nomura) and by reducing ethyl vanillylide-aceto-acetate, followed by hydrolysis (Lapworth). (*See also*, Pearson, Pharm. J. 1919, 103, 78.)

IV. *Aromatic Ketones.*

Diphenylketone (Benzophenone)

$$C_6H_5{\cdot}CO{\cdot}C_6H_5$$

This ketone is obtained by several of the general methods (2, 4, 6, 7, 10, 11, 16).

Preparation.—(i.) Dry calcium benzoate mixed with one tenth of its weight of lime is distilled from an iron retort. The distillate is fractionated, the portion distilling at 290°–310° being collected separately. This for the most part solidifies on cooling, liquid impurities are removed by pressure, and the ketone crystallised from alcohol. The yield amounts to about one-fourth of the weight of the calcium benzoate used, the other products of distillation consisting of benzene, diphenyl, and anthraquinone.

(ii.) A mixture of equivalent amounts of benzene and benzoyl chloride dissolved in carbon disulphide is treated with aluminium chloride, equal in weight to the benzoyl chloride used. The reaction is completed under reflux on the water-bath, water is carefully added, and carbon disulphide, unattacked benzene, and benzoic acid removed in a current of steam. The residual oil is washed successively with dilute hydrochloric acid, dilute caustic soda and water, dried, and fractionated. Yield 70–75 p.c.

(iii.) Well-cooled benzene is saturated with carbonyl chloride, and aluminium chloride added in small quantities at a time. The operation is conducted under reflux, and the product worked up as in the last case. From 100 grams of benzene, 55 grams of phosgene and 36 grams of aluminium chloride, 33 grams of benzophenone may be obtained.

Properties.—Rhombic prisms; m.p. 48°–49°. An unstable allotropic form (? monoclinic), melts at 26°–27° (Zincke, Annalen, 1871, 159, 377; Oechsner de Coninck, Compt. rend. 1900, 130, 40); b.p. 306° (170° at 15 mm.). Tammann has described a third modification, m.p. 45°–48°; and Walther and Wahl a fourth, m.p. −51° (Chem. Zeit. 1913, i, 313). For variation of boiling-point with pressure, *see* Crafts (Bull. Soc. chim. 1883, [ii.] 382). *Oxime* $(C_6H_5)_2C:NOH$; m.p. 139·5°–140°; *phenylhydrazone* $(C_6H_5)_2C:N{\cdot}NH{\cdot}C_6H_5$; m.p. 137°.

Arylimines (Reddelien, Ber. 1909, 42, 4759; 1910, 43, 2476).

Nitrate, yellow in colour. Other salts have not been isolated, but their existence is probable (K. H. Meyer, Ber. 1910, 43, 157).

Addition products $CO(C_6H_2)_2,AlCl_3$, m.p. 130°, and $CO(C_6H_5)AlBr_3$, m.p. 142° (Menschutkin, J. Russ. Phys. Chem. Soc. 1910, 42, 1298). The addition product with sodamide yields benzamide on decomposition with water

$$C(C_6H_5)_2(ONa)(NH_2)+H_2O \\ = C_6H_5CONH_2+C_6H_6+NaOH$$

(Haller and Bauer, Compt. rend. 1908, 147, 824). Benzophenone reacts with benzyl acetate in sunlight, giving the monoacetyl derivative of triphenylethylene glycol (Paternò and Forli-Forti, Gazz. chim. ital. 1910, 40, ii, 332).

The ketone gives benzhydrol $(C_6H_5)_2CH(OH)$ when reduced with sodium amalgam, but it is preferable to add zinc dust to an alcoholic solution to which a small amount of aqueous potash has been added (Elbs, J. pr. Chem. 1886, [ii] 33, 184).

The influence of substituents on the reduction of substituted benzophenones has been examined by Montagne and van Charante (Rec. trav. chim. 1912, 31, 298; 1917, 36, 258). For further information as to the mechanism of this reaction in presence of hydroxyl ions, *see* Böeseken and Cohen (Proc. K. Akad. Wetensch. Amsterdam, 1914, 16, 962).

Substitution (halogen, nitro, amino, &c.) derivatives are known; of these the amino and especially the dialkylamino derivatives are of considerable technical importance.

p-**Aminobenzophenone** $C_6H_5\cdot CO\cdot C_6H_4\cdot NH_2$.

(i.) 75 grams of phthalanil $C_6H_4<\substack{CO\\CO}>N\cdot C_6H_5$ and 50 grams of benzoyl chloride are boiled for 10 or 12 hours, zinc chloride (1 gram) being added from time to time. The resulting phthalylbenzoanilide $C_6H_4<\substack{CO\\CO}>N\cdot C_6H_4\cdot CO\cdot C_6H_5$ may be purified by crystallisation from glacial acetic acid; when hydrolysed by alcoholic potash it gives *p*-aminobenzophenone (benzoaniline) and phthalic acid (Doebner, Annalen, 1881, 210, 268).

(ii.) Aniline and 2 molecular proportions of benzoyl chloride are heated gradually at 220°–230°, and the temperature maintained for 20 hours. The dibenzanilide first produced is thus isomerised to a mixture of *o*- and *p*-benzoylaminobenzophenones; the change may be aided by the addition of 10 p.c. of zinc chloride. After hydrolysis of the product the two aminobenzophenones may be separated by steam distillation, the ortho- compound being volatile. Calculated on the weight of aniline used, 15 p.c. of the ortho- and 45 p.c. of the para- derivatives are obtained (Chattaway, Chem. Soc. Trans. 1004, 85, 394).

Shining leaflets; m.p. 124°.

Aminobenzophenone and dimethyl- and diethylaminobenzophenones, as well as dimethylaminobenzophenone sulphonic acid condense with pyrogallol in acid solution to form triphenylmethane mordant dyestuffs (Ges. f. Chem. Ind. Basel, D. R. P. 58689).

p-**Dimethylaminobenzophenone**

$$C_6H_5\cdot CO\cdot C_6H_4N(CH_3)_2$$

is obtained from malachite green and concentrated hydrochloric acid at 250° (Ber. 1880, 13, 2225), and by methylation of *p*-aminobenzophenone (Doebner, Annalen, 1881, 210, 270). Technically, it is more easily prepared by interaction of benzanilide, dimethylaniline, and phosphoryl chloride, and hydrolysis of the resulting product:

$$C_6H_5\cdot CO\cdot NH\cdot C_6H_5 \rightarrow C_6H_5\cdot CCl:N\cdot C_6H_5 \\ \rightarrow C_6H_5\cdot C(C_6H_4\cdot N[CH_3)_2]:N\cdot C_6H_5 \\ \rightarrow C_6H_5\cdot CO\cdot C_6H_4\cdot N(CH_3)_2$$

20 kilos. benzanilide, 40 kilos. dimethylaniline, and 20 kilos. phosphoryl chloride are stirred and warmed until spontaneous heating takes place, the temperature is then kept below 120°, and the reaction subsequently finished by one or two hours' heating on the water-bath.

Hydrolysis may be effected in one of two ways:

(*a*) The mass is poured into 100 litres of water and 5 kilos. of hydrochloric acid warmed to 50°, the liquid allowed to stand, whereby a portion of the ketone separates, the remainder being precipitated by the addition of 500 litres of water and careful neutralisation with caustic soda. The ketone is collected, extracted with hydrochloric acid, washed, and dried.

(*b*) The mass is made alkaline, excess of dimethylaniline removed in a current of steam, and the granular residue hydrolysed at 50°–70° with 100 litres of water and 10 kilos. of hydrochloric acid. A portion of the ketone is precipitated, the remainder is obtained by addition of aqueous caustic soda, care being taken not to throw the aniline out of solution. Other dialkylaminobenzophenones may be similarly obtained (Farb. vorm. Meister, Lucius, and Bruning, D. R. PP. 41751, 42853).

p-Dimethylaminobenzophenone forms colourless leaflets; m.p. 90°–91°. It is a weak base, insoluble in water, sparingly soluble in cold alcohol. Phosphorus trichloride yields a yellow compound, probably

$$C_6H_5\cdot CCl_2\cdot C_6H_4\cdot N(CH_3)_2 \text{ or } \\ C_6H_5\cdot CCl:C_6H_4:N(CH_3)_2Cl$$

which can be purified by solution in chloroform and reprecipitation by petroleum spirit. It is easily converted into the original ketone by heating with water, and condenses directly with dimethylaniline, forming malachite green (B. A. S. F., D. R. P. 27789).

The hydrol $C_6H_5\cdot CH(OH)\cdot C_6H_4\cdot N(CH_3)_2$ (m.p. 69°–70°), obtained by reduction of dimethylaminobenzophenone, condenses with dimethylaniline to leuco malachite green.

If the reduction is carried out electrolytically or by zinc and sulphuric or hydrochloric acid, the corresponding pinacone, m.p. 196°, is found. This yields a mixture of the ketone and hydrol when heated with alcoholic potash (Fischl, Monatsh. 1913, 34, 337).

Michler's ketone reacts with the Grignard reagents, malachite green can be obtained in this way (Votoček, Ber. 1913, 46, 1755, 1760).

4 : 4′-**Diaminobenzophenone**

$$NH_2\cdot C_6H_4\cdot CO\cdot C_6H_4\cdot NH_2$$

(m.p. 172°), and its trimethyl derivative $(CH_3)_2N\cdot C_6H_4\cdot CO\cdot C_6H_4\cdot NH(CH_3)$ (m.p. 156°) are obtained from pararosaniline (or rosaniline) and pentamethyl violet, respectively by prolonged heating with hydrochloric acid (Wichelhaus, Ber. 1886, 19, 109)

Diaminobenzophenone and its derivatives can be condensed with pyrogallol to green or blue mordant dyestuffs (Ges. f. chem. Ind. Basel, D. R. P. 61326).

Tetramethyldiaminobenzophenone (Michler's ketone) $CO[C_6H_4·N(CH_3)_2]_2$ is a valuable intermediate product in the preparation of many dyestuffs, and was first obtained by Michler (Ber. 1876, 9, 716, 1900). Dimethylaniline is saturated at ordinary temperature with the theoretical quantity of phosgene, and the reaction completed by warming in a closed vessel to 100°. Water is added, excess of dimethylaniline removed by steam distillation, and the ketone purified from adherent blue colouring matter by repeated solution in hydrochloric acid and reprecipitation with soda.

Michler's ketone may also be prepared by carefully heating on the water-bath 10 kilos. of dimethylaminobenzanilide

$$(CH_3)_2N·C_6H_4·CO\,NH·C_6H_5$$

18 kilos. of dimethylaniline, and 8·5 grams of phosphoryl chloride, the product being worked up in a similar manner to that adopted in the case of dimethylaminobenzophenone.

Disubstituted dialkylaminobenzamides (Meister, Lucius, Brüning, D. R. P. 44238) may also be employed. Thus 10 kilos. of dimethylaminobenzodiphenylamine $(CH_3)_2N·C_6H_4·CO\,N(C_6H_5)_2$, 12 kilos. of dimethylaniline, and 5 kilos. of phosphoryl chloride are heated on the water-bath for 2 hours; the product being subsequently worked up by hydrolysis with hydrochloric acid, precipitation of the ketone and diphenylamine and separation of the latter by washing with alcohol (D. R. P. 44077).

The ketone forms silvery leaflets, m.p. 174° (corr.), boils with some decomposition above 360°; it is easily soluble in alcohol and ether. The basic properties are weak. *Picrate*

$$C_{17}H_{20}ON_2,C_6H_2(OH)(NO_2)_3$$

m.p. 156°–157°.

Tetraethyldiaminobenzophenone obtained similarly melts at 95°–96° (Michler and Gradman, Ber. 1876, 9, 1914).

Replacement of oxygen in the above ketones by the imino group gives auramines (*q.v.*).

In presence of condensing agents (*e.g.* $POCl_3$, $COCl_2$, &c.) the tetralkyldiaminobenzophenones condense with aromatic amines to give dyestuffs of the triphenyl (diphenylnaphthyl, &c.) series, but cleaner products are generally obtained by reducing the ketones to hydrols, and condensing these with amines, &c., to leuco-compounds, which are subsequently oxidised to the corresponding dyestuffs.

Reduction to hydrols may be effected by sodium amalgam in alcoholic solution; technically zinc dust and caustic soda in amyl alcoholic solution are employed (B. A. S. F., D. R. P. 27032). Tetramethyldiaminobenzhydrol dissolves in acetic acid with an intense blue colour, which is discharged on rendering alkaline.

Amino (and acetamino) derivatives of tetra-alkyldiaminobenzophenones may be obtained from nitro derivatives by reduction. Michler's ketone, when nitrated, gives 3-nitro- and 3 : 3′-dinitro-4 : 4′- tetramethyldiaminobenzophenone (Kliegl, Ber. 1906, 39, 1266); the latter compound has also been obtained by the action of dimethylamine on 3 : 3′-dinitro-4 : 4′-dichlorobenzophenone (Consonn[illegible] Gazz. chim. ital. 1904, 34, i. 386). Introduction of the nitro group in position 2 may be effected by nitrating tetramethyldiaminodiphenylmethane, and subsequently oxidising the CH_2 group (Farbenf. vorm. Fr. Bayer & Co., D. R. P. 79250).

Hydroxyl derivatives of Benzophenone.

Numerous hydroxyl derivatives of benzophenone have been prepared, many by reactions involving the condensation of benzoic acid and its derivatives with phenols:

$$C_6H_{5-x}(OH)_xCOOH+C_6H_{6-y}(OH)_y$$
$$=C_6H_{5-x}(OH)_xCO·C_6H_{5-y}(OH)_y+H_2O$$

The trihydroxybenzophenones obtained from pyrogallol contain the grouping

$$·CO·C_6H_2(OH)_3(CO : OH : OH : OH = 1 : 2 : 3 : 4)$$

they are generally yellow in colour, and are used as mordant dyestuffs.

Alizarin yellow A, $C_6H_5·CO·C_6H_2(OH)_3$, is obtained by heating 1 part of pyrogallol and 1 part of benzoic acid to 145°, and adding 3 parts of zinc chloride with continuous stirring. The end of the reaction, which takes about 3 hours to complete, is recognised by the solution of the product in hot water giving slender bright yellow needles, and not benzoic acid on cooling. The mass is dissolved in 60 parts of boiling water, boiled 2 hours with animal charcoal, filtered, and allowed to crystallise. It forms yellow needles (with $1H_2O$); m.p. 137°–138°. *Acetyl* derivative, colourless; m.p. 119°. On cotton mordanted with alumina it dyes golden-yellow shades, which incline to orange in presence of calcium salts. A fine yellow is produced with aluminium acetate and tin salt; the chromium lake is brownish-yellow, and the iron lake dark olive. The colours produced are very fast.

Dyestuffs giving similar shades are produced by the condensation of pyrogallol with *m*- and *p*-hydroxybenzoic acid, and β-resorcylic acid; those from pyrogallol and salicylic or pyrogallol-carboxylic acids give redder lakes, whilst the lakes are of a greenish-yellow shade if dyestuffs obtained by condensing gallic acid with resorcinol or pyrogallol are employed. The chemistry of these hydroxyketone dyestuffs has been studied by C. Graebe and A. Eichengrün (Annalen, 1892, 269, 295).

New dyestuffs, greener in shade, are obtained by fusing alizarin yellow A or C with the ammonium salts of organic acids (Prud'homme, Rev. gén. Mat. col. 1906, 10, 225).

Two unsaturated aromatic ketones, the benzalacetones, have been described under general methods of preparation (No. 18).

Thioketones.

Thiobenzophenone $C_6H_5·CS·C_6H_5$ was first obtained by Bergreen (Ber. 1886, 21, 341) in an impure condition by the action of 2 parts of aluminium chloride on 1 part of thiophosgene ($CSCl_2$) dissolved in 5 parts of benzene, the reaction being completed on the water-bath. After treatment with ice, and extraction with ether, the ethereal solution was washed with soda and water, and the ether distilled off, the thioketone remaining as an oil.

L. Gattermann and H. Schulze (Ber. 1896, 29, 2944) found that it is impossible to obtai the thioketone in a pure condition by th method, but were successful in treating benzophenone chloride $C_6H_5\cdot CCl_2\cdot C_6H_5$ with very slightly over the theoretical quantity of alcoholic potassium sulphide. The mixture becomes hot, potassium chloride separates, and the solution assumes a blue colour. After cooling, water is added, the thioketone extracted with ether, the latter distilled off, and the product fractionated under reduced pressure. The thioketone passes over at 174° (14 mm.) as a deep blue oil, which solidifies to long blue needles.

Thiobenzophenone is very unstable, and can only be preserved in sealed tubes filled with carbon dioxide. Its colour is discharged on warming with alcoholic potash, benzophenone being regenerated; it reacts with hydroxylamine giving benzophenone-oxime, and on heating with copper powder gives tetraphenylethylene.

Gattermann has also described corresponding alkyloxythioketones obtained by the action of thiophosgene on anisole, phenetole, *o*-cresyl ethyl ether, *o*-cresyl methyl ether, *o*-chloroanisole, *o*-chlorophenetole, and *o*-bromoanisole. The compounds obtained resemble thiobenzophenone in their reactions (Ber. 1895, 28, 2869)

On account of the greater reactivity of the :C:S group as compared with carbonyl, the sulphur analogue of Michler's ketone has been prepared by several methods.

Tetramethyldiaminothiobenzophenone

$$(CH_3)_2N\cdot C_6H_4\cdot CS\cdot C_6H_4\cdot N(CH_3)_2$$

Preparation.—(i.) 5 parts of dimethylaniline are cooled to 0°-10°, and 1 part of thiophosgene in 3 parts of carbon disulphide added in the course of 3 or 4 hours with continual stirring, which is continued for 10-12 hours without further cooling. Alkali is added, carbon disulphide and dimethylaniline removed in a current of steam, and the thioketone crystallised (Kern, D. R. P. 37730).

(ii.) An intimate mixture of Michler's ketone and one-fifth of its weight of phosphorus pentasulphide is heated not above 160°. The mass is exhausted successively with water, very dilute sodium carbonate solution and water, and finally crystallised from amyl alcohol (B. A. S. F., D. R. P. 39074).

(iii.) 100 parts of Michler's ketone, 38 parts of phosphoryl chloride, and 400 parts of toluene are heated on a water-bath and hydrogen sulphide led in until a test specimen no longer dissolves in water with a blue colour; or

37 parts of phosgene are passed into a solution of 100 parts of Michler's ketone in 400 parts of chloroform at 15°-20°, after the evolution of carbon dioxide has ceased, 90 parts of sodium sulphide in 800 parts of water are added. The solvent is removed by steam distillation, and the thioketone crystallised from alcohol (B. A. S. F., D. R. P. 40374).

(iv.) An alcoholic solution of auramine base is saturated with hydrogen sulphide, first in the cold, then on the water-bath (Fehrmann, Ber. 1887, 20, 2857; Graebe, *ibid.* 3267).

Properties.—M.p. 202°. Fairly soluble in chloroform, sparingly so in cold alcohol or ether. Yields Michler's ketone on warming with hydrochloric acid.

The chemistry of this ketone has also been studied by Staudinger and Siegwart (Helv. Chim. Acta, 1920, 3, 833).

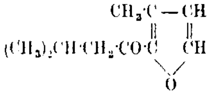
Pyridine and Quinoline Ketones.

Ketones containing a carbonyl group united on the one hand to a hydrocarbon radicle (alkyl or acyl) and on the other to a pyridine or quinoline residue are known. Thus picolinoyl chloride may be condensed with benzene in presence of a small amount of thionyl chloride to give 2-*pyridyl phenyl ketone*, b.p. 182°/14 mm. (*Wolffenstein and Hartwich, Ber.* 1915, 48, 2043).

Ketones containing quinoline residues are interesting on account of their relationship to alkaloids of the cinchona group, and of their physiological properties. The 4-quinolyl ketones have been specially studied (A. Kaufmann, Ber. 1912, 45, 3090; 1913, 46, 57, 2929; D. R. P. 268931; Rabe, Ber. 1913, 46, 1026, 1032; 1917, 50, 144; Vereinigte Chininfabriken Zimmer & Co., D. R. PP. 268830, 280970, 330915; Howitz and Kopke, Annalen, 1913, 396, 38).

FURANE AND PYRROLE KETONES, ETC.

Ketones derived from furane are known, thus Esholtzione has the structure



(Michizo Asano, J. Pharm. Soc. Japan, 1919, 454, 999). Related compounds may be obtained by the action of magnesium alkyl halides on pyromuconitrile (K. Monoya, *ibid.* 447, 357).

Dipyrryl ketone, $(C_4H_3NH)_2CO$, and pyrrolic ketonic acids have been described by B. Oddo (Gazzetta, 1920, 50, ii. 258).

Thionyl ketones are described by Steinkopf and Schubart (Annalen, 1921, 424, 1).

OPEN CHAIN DIKETONES.

The diketones are most conveniently classified according to the relative positions of the carbonyl groups in the carbon chain. Thus they may be divided in the following way:—

1 : 2- or *α*-diketones $R\cdot CO\cdot CO\cdot R'$.
1 : 3- or *β* diketones $R\cdot CO\cdot CH_2\cdot CO\cdot R'$.
&c. &c.

1 : 2- *or α-Diketones.*

Preparation.—(1) The *α*-diketones may be obtained as monoximes by the action of nitrous acid on monoketones or *β*-ketonic esters:

$$R\cdot CO\cdot CH_2\cdot R' + HNO_2 = H_2O + R\cdot CO:(NOH)\cdot R'$$
$$R\cdot CO\cdot CHR'\cdot CO_2C_2H_2 + HNO_2$$
$$= CO_2 + C_2H_5OH + R\cdot CO\cdot C(:NOH)\cdot R'$$

The monoximes of the 1 : 2-diketones can often be prepared by the action of diazonium salts on alkaline solutions of *iso*nitrosoacetone (Borsche, Ber. 1907, 40, 707):

$$C_6H_5N_2Cl + NaON:CH\cdot CO\cdot CH_3$$
$$= C_6H_5\cdot C(:NOH)\cdot CO\cdot CH_3 + NaCl + N_2$$

The results with *iso*nitrosoacetophenone are not so favourable.

The replacement of the *iso*nitroso- group by oxygen may be effected:

(i.) By boiling with dilute sulphuric acid (v.

Pechmann, Ber. 1887, 20, 3213; 1888, 21, 1411).

$$CH_2\cdot CO\cdot C(:NOH)\cdot CH_3+H_2O \\ =CH_3\cdot CO\cdot CO\cdot CH_3+H_2NOH$$

(ii.) By conversion into salts of iminosulphonic acids by the action of alkaline bisulphites, and subsequently hydrolysing by boiling with *15 p.c. sulphuric acid* :

$$CH_3\cdot CO\cdot C(:NOH)\cdot CH_3+NaHSO_3 \\ =CH_3\cdot CO\cdot C(:N\cdot SO_3Na)\cdot CH_3+H_2O$$

$$CH_3\cdot CO\cdot C(:N\cdot SO_3H)\cdot CH_3+2H_2O \\ =CH_3\cdot CO\cdot CO\cdot CH_3+(NH_4)HSO_4$$

(v. Pechmann, Ber. 1887, 20, 3162; 1889, 22, 2115).

(iii.) By warming with *isoamyl* nitrite (Manasse, Ber. 1888, 21, 2177):

$$CH_3\cdot CO\cdot C(:NOH)\cdot CH_3+C_5H_{11}\cdot ONO \\ =CH_2\cdot CO\cdot CO\cdot CH_3+C_5H_{11}OH+N_2O$$

Similarly diethyl acetosuccinate gives *iso*nitrosolævulic acid, the latter compound yielding diacetyl on boiling with dilute sulphuric acid (Thal, Ber. 1892, 25, 1723).

The mixed aliphatic-aromatic diketones are obtained in a similar way from mixed *iso*nitrosoketones (v. Pechmann and Muller, Ber. 1888, 21, 2119; 1889, 22, 2128).

(2) Ketones of the structure $CH_3\cdot CO\cdot CH_2R$, when warmed with nitric acid (sp.gr. 1·38) give ketones $CH_3\cdot CO\cdot CO\cdot R$ (Fileti and Ponzio, Gazz. chim. ital. 1895, 25, i. 233).

(3) Aromatic (and some heterocylic) diketones are obtained from aldehydes $R\cdot CHO$ by condensation to the keto alcohols

$$R\cdot CO\cdot CH(OH)\cdot R$$

under the influence of potassium cyanide and subsequent oxidation with chlorine (Laurent, Annalen, 1836, 17, 91), or more frequently nitric acid (Zinin, *ibid.* 1840, 34, 188).

(4) By heating compounds of the type $R\cdot CBr:CBr\cdot R$ with water to 200° (*e.g.* tolane bromide) (Limpricht and Schwanert, Ber. 1871, 4, 380):

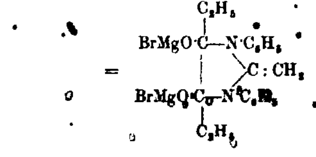
$$2C_6H_5\cdot CBr:CBr\cdot C_6H_5+2H_2O \\ =C_6H_5\cdot CO\cdot CO\cdot C_6H_5+C_6H_5\cdot C:C\cdot C_6H_5+4H_2O$$

(5) By hydrolysis of compounds

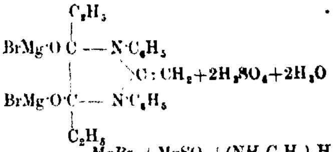
$$R\cdot CX_2\cdot CX_2\cdot R$$

(X = halogen). Thus tolane tetrachloride, when heated with sulphuric acid to 165°, or with glacial acetic acid to 230°–250° (Liebermann and Homeyer, Ber. 1879, 12, 1075).

(6) The vinylidene-oxanilide prepared by v. Pechmann by 8 hours boiling of 1 part of oxanilide, 1 part of fused sodium acetate, and 10 parts of acetic anhydride (Ber. 1897, 30, 2791) reacts readily with the Grignard reagents, forming compounds which furnish diketones on decomposition with dilute sulphuric acid:



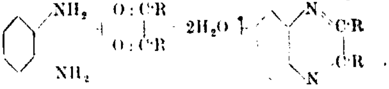
$$\begin{array}{l} CO\cdot N\cdot C_6H_5 \\ \qquad >C:CH_2+2C_2H_5MgBr \\ CO\cdot N\cdot C_6H_5 \end{array} = \begin{array}{l} \quad C_2H_5 \\ BrMgO\cdot C—N\cdot C_6H_5 \\ \qquad\qquad >C:CH_2 \\ BrMgO\cdot C—N\cdot C_6H_5 \\ \quad C_2H_5 \end{array}$$



$$\begin{array}{l} \quad C_2H_5 \\ BrMg\cdot O\cdot C—N\cdot C_6H_5 \\ \qquad\qquad >C:CH_2+2H_2SO_4+2H_2O \\ BrMg\cdot O\cdot C—N\cdot C_6H_5 \\ \quad C_2H_5 \end{array} \\ =MgBr_2+MgSO_4+(NH_2C_6H_5)_2H_2SO_4 \\ +CH_3\cdot COOH+C_2H_5\cdot CO\cdot CO\cdot C_2H_5$$

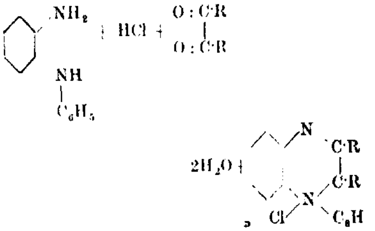
(L. Tschugaeff, Ber. 1907, 40, 186).

General properties and reactions.—(1) The most characteristic reaction of the α-diketones is their condensation with aromatic *o*-diamines to quinoxalines:

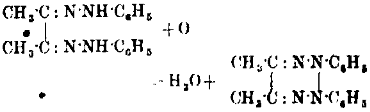


The resulting coloured compounds crystallise well, have definite melting-points, and are readily identified (Hinsberg, Ber. 1884, 17, 322; Annalen, 1887, 237, 327).

When monosubstituted *o*-diamines are employed, salts of ammonium type are produced:

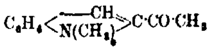


(2) Phenylhydrazine gives *mono-* or *di*hydrazones; for preparation of the former, *see* Petrenko-Kritschenko and Eltschaninoff (Ber. 1901, 34, 1699). The dihydrazones (usually called osazones) derived from aliphatic diketones or diketones containing only one aromatic radicle, are readily oxidised by ferric chloride to red or brown osotetrazones (v. Pechmann, Ber. 1888, 21, 2751):



$$\begin{array}{l} CH_3\cdot C:N\cdot NH\cdot C_6H_5 \\ CH_3\cdot C:N\cdot NH\cdot C_6H_5 \end{array} +O = H_2O + \begin{array}{l} CH_3\cdot C:N\cdot N\cdot C_6H_5 \\ CH_3\cdot C:N\cdot N\cdot C_6H_5 \end{array}$$

Diacetylphenylmethylhydrazone condenses when shaken with warm hydrochloric acid to 2-acetyl-1-methylindole



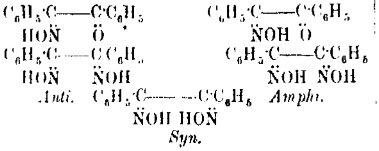
$$C_6H_4<\begin{array}{c} CH \\ N(CH_3) \end{array}>C\cdot CO\cdot CH_3$$

(Diels and Kollisch, Ber. 1911, 44, 263). From this hydrazone and magnesium alkyl halides, keto-alcohols are obtainable when the phenylmethylhydrazine is again removed (Diels and Joblin, Ber. 1911, 44, 403).

For action of hydrazine *v.* Curtius and Kastner, J. pr. Chem. 1911, 83, 215.

(3) Hydroxylamine yields *mono-* or *di*oximes, the former can exist in two, the latter

in three modifications, even when the original diketone is symmetrical in structure:



$$\begin{array}{ll} \mathrm{C_6H_5{\cdot}C{-}{-}C{\cdot}C_6H_5} & \mathrm{C_6H_5{\cdot}C{-}{-}C{\cdot}C_6H_5} \\ \quad\mathrm{HO\ddot{N}\quad \ddot{O}} & \quad\mathrm{\ddot{N}OH\quad \ddot{O}} \\ \mathrm{C_6H_5{\cdot}C{-}{-}C{\cdot}C_6H_5} & \mathrm{C_6H_5{\cdot}C{-}{-}C{\cdot}C_6H_5} \\ \quad\mathrm{HO\ddot{N}\quad \ddot{N}OH} & \quad\mathrm{\ddot{N}OH\quad \ddot{N}OH} \\ \textit{Anti.} & \textit{Amphi.} \end{array}$$

$$\begin{array}{c} \mathrm{C_6H_5{\cdot}C{-}{-}C{\cdot}C_6H_5} \\ \mathrm{\ddot{N}OH\quad HO\ddot{N}} \\ \textit{Syn.} \end{array}$$

(K. Auwers and V. Meyer, Ber. 1888, 21, 810; 1889, 22, 705; A. Hantzsch and A Werner, Ber. 1890, 23, 11) The *syn*dioximes are characterised by the ease with which they lose water yielding furazane derivatives.

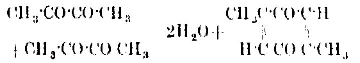
The discovery of a fourth benzildioxime cannot be reconciled with the stereochemical formulation (Atack and Whinyates, Trans. Chem. Soc. 1921, 119, 1184).

(4) Semicarbazide gives *mono-* and *di-*semicarbazones and cyclic condensation products (*see* Thiele, Annalen, 1894, 283, 37; Posner, Ber. 1901, 34, 3973; Biltz and Arnd. *ibid.* 1902, 35, 344; Diels, *ibid.* 1902, 35, 347).

(5) With caustic potash the aromatic α-diketones yield diaryl glycollic acids (Liebig, Annalen, 1838, 25, 25; Zinin, *ibid.* 1839, 31, 329):

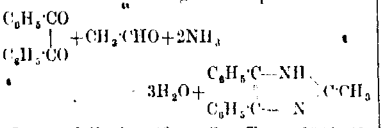
$$\mathrm{C_6H_5{\cdot}CO{\cdot}CO{\cdot}C_6H_5 + KOH = (C_6H_5)C(OH)COOK}$$

The aliphatic α-diketones, however, when warmed in alkaline solution undergo condensation with formation of quinones; thus diacetyl gives xyloquinone (v. Pechmann, Ber. 1888, 21, 1417):



$$\begin{array}{lcl} \mathrm{CH_3{\cdot}CO{\cdot}CO{\cdot}CH_3} & & \mathrm{CH_3{\cdot}C{\cdot}CO{\cdot}C{\cdot}H} \\ & \mathrm{2H_2O+} & \\ \mathrm{+\,CH_3{\cdot}CO{\cdot}CO{\cdot}CH_3} & & \mathrm{H{\cdot}C{\cdot}CO{\cdot}C{\cdot}CH_3} \end{array}$$

(6) With aldehydes and ammonia, glyoxalines are formed amongst other products:



$$\begin{array}{l} \mathrm{C_6H_5{\cdot}CO} \\ \quad| \quad \mathrm{+CH_3{\cdot}CHO+2NH_3} \\ \mathrm{C_6H_5{\cdot}CO} \end{array} = \mathrm{3H_2O+} \begin{array}{l} \mathrm{C_6H_5{\cdot}C{-}NH} \\ \qquad\qquad\quad \mathrm{>C{\cdot}CH_3} \\ \mathrm{C_6H_5{\cdot}C{-}{-}N} \end{array}$$

(Japp and Hooker, Chem. Soc. Trans. 1884, 45, 672; Japp and Wynne, *ibid.* 1886, 49, 164).

1 : 3- or β- *Diketones.*

The lowest member of the series, acetylacetone, or 2 : 4-pentanedione, was obtained by Combes by the action of aluminium chloride on acetyl chloride and decomposition of the resulting crystalline substance $\mathrm{C_{12}H_{14}O_6Al_2Cl_8}$ with water (Compt. rend. 1886, 103, 814).

The usual method of preparation of the 1 : 3-diketones is given under general reaction 17 of monoketones (*vide supra*). As condensing agents for bringing about the reaction

$$\mathrm{R{\cdot}CO{\cdot}OC_2H_5+CH_3{\cdot}CO{\cdot}R'}$$
$$\mathrm{\rightarrow R{\cdot}C(ONa):CH{\cdot}COR' \rightarrow R{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}R'}$$

Claisen has found that alcoholic sodium ethoxide works most feebly and in order of increasing activity, are anhydrous sodium ethoxide, metallic sodium (Annalen, 1894, 277, 168, and sodium amide (Ber. 1905, 38, 695).

The sodium derivatives are represented above as derived from enols. Knorr (Ber. 1911, 44, 2767) has isolated the enolic form of acetylacetone, m.p. −9°, n_D^{15} 1·4609. K. H. Meyer and Hopff find n_D^{10} 1·4625 (Ber. 1921, 54, 579). This is transformed at 15° into the allelotropic mixture of diketone and enol-ketone, n_D^{15} 1·4550, the change being complete in 20 minutes (*cf.* for enolisation of benzoylacetone, Smedley, Chem. Soc. Trans 1910, 97, 1486; Scheiber, Ber. 1913, 46, 1100, 1105).

Unsaturated β-diketones have been prepared by Ryan (Proc Roy. Irish Acad. 1913, 32, B, 1, 9; 1916, 35, B, 199).

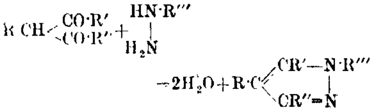
General properties and reactions.—(1) The 1 : 3-diketones form stable metallic derivatives. Acetylacetone, for example, forms compounds of the types $\mathrm{Mn^{II}(C_5H_7O_2)_2}$, $\mathrm{Mn^{III}(C_5H_7O_2)_3}$, &c., many of which are volatile without decomposition, and may be used for vapour density determinations, thus controlling the valencies of several metals; *e.g.* divalent Gl and Cu, and trivalent Al, Fe, Mn, Co, and Cr (A. Combes, Compt. rend. 1896, 119, 1221; Bull. Soc. chim. 1889, [iii.] 1, 345; Urbain and Debierne, Compt. rend. 1899, 129, 302; Claisen, Ber. 1889, 22, 1010; Annalen, 1893, 277, 170; Morgan, Chem. Soc. Trans. 1913, 103, 81; 1914, 105, 189; 1921, 119, 610, 1058; Weinland and Bässler, Zeitsch. anorg. Chem. 1916, 96, 109). The metallic radicle may be replaced by acyl groups, branched triketones resulting from the reaction:

$$\mathrm{C_6H_5{\cdot}C(ONa):CH{\cdot}CO{\cdot}C_6H_5+C_6H_5COCl}$$
$$\mathrm{= NaCl+(C_6H_5CO)_3CH}$$

(v. Baeyer and Perkin, Ber. 1883, 16, 2128; L. Claisen, Ber 1894, 27, 111; Annalen, 1896, 291, 25; Ber. 1904, 36, 3674).

Morgan regards the polyvalent metallic compounds of acetylacetone as coordination derivatives. In this connection, it may be noted that β-diketones occupy two positions at the central atom and acetylacetonatediethylenediamine cobalt salts have been resolved into optically active forms (Werner, Schwyzer and Karrer, Helv. Chim. Acta, 1921, 4, 113).

(2) On warming with arylhydrazines, pyrazoles are produced:



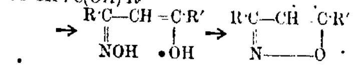
$$\mathrm{R{\cdot}CH}\begin{array}{l}\mathrm{<CO{\cdot}R'} \\ \mathrm{\ \ CO{\cdot}R''}\end{array} + \begin{array}{c}\mathrm{HN{\cdot}R'''} \\ | \\ \mathrm{H_2N}\end{array} = \mathrm{2H_2O+R{\cdot}C}\begin{array}{l}\mathrm{{=}CR'{-}N{\cdot}R'''} \\ \qquad\qquad | \\ \mathrm{\ CR''{=}N}\end{array}$$

(L. Knorr, Ber. 1885, 18, 311; Annalen, 1887, 238 37). This reaction can be utilised as the basis of a colour test for β-diketones since pyrazoles are reduced by sodium in boiling alcoholic solution to pyrazolines. If when solution of the metal is complete, water be added and the alcohol boiled off, the pyrazoline may be extracted with ether, and is left when the solvent is evaporated. If the residue be dissolved in fairly concentrated sulphuric acid, addition of a drop of solution of sodium nitrite or potassium dichromate produces a beautiful coloration varying from fuchsine red to blue. This reaction, which can be carried out in test tubes, is general for all pyrazoles derived from phenylhydrazine, not, however, for those obtained from hydrazine itself (L. Knorr, Ber. 1885, 18, 2259; 1893, 26, 101; Annalen, 1887, 238, 200).

(3) Semicarbazide gives similar pyrazole derivatives (T. Posner, Ber. 1901, 34, 3973).

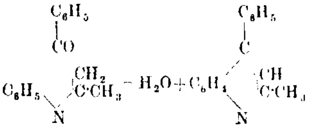
(4) With hydroxylamine the 1 : 3-diketones behave as if one of the ketonic groups were enolised and furnish isoxazoles :

R·CO·CH : C(OH)·R′



(Combes, Ann. Chim. 1887, [vi.] 12, 215; Zedel, Ber. 1888, 21, 2178; Claisen, *ibid.* 1891, 24, 3907).

(5) Aniline and benzoylacetone lose 1 molecule of water at 150°, a second molecule of water is removed by heating with concentrated sulphuric acid, α-methyl-γ-phenylquinoline being formed (C. Beyer, Ber. 1887, 20, 1770; Combes, Bull. Soc. chim. 1888, [ii.] 49, 89; Rügheimer a Ritter, *ibid.* 1912, 45, 1332).



Acetanilide (not a dianil) is produced when acetylacetone is heated for a long time with a large excess of aniline (Turner, Chem. Soc. Trans 1917, 111, 1).

A compound with a seven-membered ring $C_7H_{12}N_2$ is obtained by condensation of acetylacetone with ethylene diamine (Rosanov, J. Russ. Phys. Chem. Soc. 1915, 47, 611). Condensation with benzylamine (Rügheimer, Ber. 1912, 45, 1332); with ethyl cyanoacetate (Simonsen and Nagok, Chem. Soc. Trans. 1915, 167, 794).

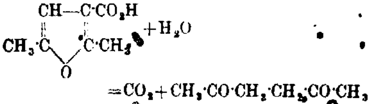
(6) β-Diketones and β-ketonic esters condense with esters of acetylenic acids, giving unsaturated diketones or ketonic esters. From these, pyrone derivatives have been obtained (Ruhemann, Chem. Soc. Trans. 1899, 75, 245, 411; 1908, 93, 431).

(7) Acetylacetone yields βδ-dihydroxypentane when reduced by sodium in absolute alcoholic solution (Bauer, Compt. rend. 1912, 154, 1092).

(8) Acetylacetone (as sodium salt) reacts with thiocarbimides to form thioanilides, such as $CH_3·CO·CH(CS·NHC_6H_5)·CO·CH_3$ yellow needles, m.p. 107°–108°. Alkalies remove an acetyl group (Worrall, J. Amer. Chem. Soc. 1920, 42, 1055).

1 : 4- *or γ-Diketones.*

Preparation.—(1) The lowest member of the series, acetonylacetone or 2 : 5-hexanedione was obtained by Paal by heating pyrotritaric acid with water at 150°–160° (Ber. 1885, 18, 58):

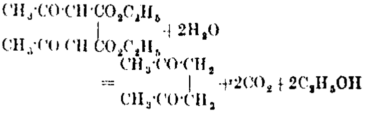


$$=CO_2+CH_3·CO·CH_2·CH_2·CO·CH_3$$

(2) α-Halogenised ketones react normally with the sodium derivative of ethyl acetoacetate : on hydrolysis 1 : 4-diketones are produced (Paal, Ber. 1883, 16, 2865) :

$$CH_3·CO·CH(COOC_2H_5)CH_2·CO·C_6H_5+H_2O$$
$$=CO_2+C_2H_5OH+CH_3·CO·CH_2·CH_2·CO·C_6H_5$$

(3) By hydrolysis of compounds of the type of diethyl diacetosuccinate, preferably with potassium carbonate solution :



$$\begin{array}{l} CH_3·CO·CH·CO_2C_2H_5 \\ \quad | \qquad\qquad +2H_2O \\ CH_3·CO·CH·CO_2C_2H_5 \end{array} = \begin{array}{l} CH_3·CO·CH_2 \\ \quad | \\ CH_3·CO·CH_2 \end{array} +2CO_2+2C_2H_5OH$$

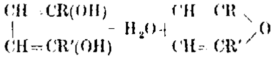
(Knorr, Ber. 1887, 20, 169, 2100; 1900, 33, 1219; Annalen, 1899, 306, 363).

Acetylenic γ-diketones, *e.g.*

$$C_6H_5·CO·C:C·CO·C_6H_5$$

m.p. 112°, have been prepared (Dupont, Compt. rend. 1914, 158, 1349).

General reactions.—(1) Reacting in the dienolic form, 1 : 4-diketones are dehydrated by fuming hydrochloric acid or acetic anhydride, yielding furfurane derivatives (Paal, Ber. 1884, 17, 2756) :



(2) Phosphorus pentasulphide converts them in a similar manner into thiophen compounds.

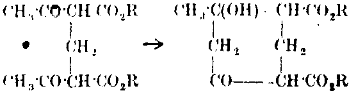
(3) Ammonia similarly yields pyrrole derivatives, whilst hydrazine yields pyridazines (Blaise, Compt. rend. 1920, 170, 1324). Semicarbazide gives disemicarbazones which are easily converted into 1-carbamidopyrroles (Compt. rend. 1921, 172, 221, 313).

1 : 5-*Diketones*, &c.

Esters of 1 : 5-diketonecarboxylic acids may be obtained by the condensation of ethyl acetoacetate with aldehydes (P. Rabe, Annalen, 1902, 323, 88; 1904, 332, 11; 1908, 360, 265; Dieckmann a. v. Fischer, Ber. 1911, 44, 966) :

$$CH_2O+2CH_3·CO·CH_2·CO_2C_2H_5$$
$$H_2O+CH_2[CH(COCH_3)·CO_2C_2H_5]_2$$

Such compounds easily undergo an intramolecular aldol-condensation, yielding 1 : 5-*cyclo*hexanolones :

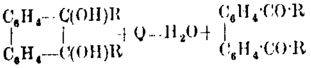


The differentiation of the isomerides is easy, derivatives of dihydropyridine and pyridine being obtained from the 1 : 5-diketonic compounds when treated with ammonia and hydroxylamine respectively.

E. Blaise and A. Koehler (Compt. rend. 1909, 148, 489; Bull. Soc. chim. 1910, iv. 7, 416, 665, 710) have utilised the organo zinc compounds in conjunction with the chlorides of dibasic acids for the synthesis of diketones with far removed carbonyl groups. Whilst succinyl and glutaryl chlorides yield γ- and δ-lactones respectively, the higher acid chlorides react in the sense :

$$COCl(CH_2)_nCOCl+2RZnI$$
$$=ZnCl_2+ZnI_2+R·CO(CH_2)_nCO·R$$

T. Zincke (Annalen, 1908, 362, 242; 363, 302) has also obtained 1 : 6-diketones by oxidising the ditertiary alcohols obtained from phenanthraquinone by the Grignard reagents :



$$\begin{array}{l} C_6H_4\text{—}C(OH)R \\ \;| \qquad\quad | \\ C_6H_4\text{—}C(OH)R \end{array} + O - H_2O + \begin{array}{l} C_6H_4{\cdot}CO{\cdot}R \\ | \\ C_6H_4{\cdot}CO{\cdot}R \end{array}$$

Heptane-$\beta\zeta$-dione

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_3$$

m.p. 33°–34°, b.p. 221°–222°, has been obtained from caoutchouc ozonide (Harries, Ber. 1914, 47, 784).

Certain hydroxy-1 : 5-diketones are claimed to be of pharmacological importance; e.g. octane-$\gamma\eta$-dione-α-ol and $\beta\zeta$-dimethyloctane-$\gamma\eta$-dione-α-ol (Bayer & Co, D. R. PP. 227176, 227177).

The enolic and ketonic forms of unsaturated 1 : 5-diketones are discussed by Dilthey and Böttler (Ber. 1919, 52, 2040) in reference to their conversion to pyrylium compounds.

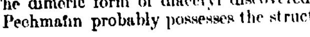
1 : 6-Diketones are also known, e.g. $\alpha\delta$-dibenzoylbutane (Bauer, Compt. rend. 1912, 155, 285)

Individual Open-chain Diketones.

Diacetyl $CH_3{\cdot}CO{\cdot}CO{\cdot}CH_3$ may be prepared by the method of O. Diels and E. Stephan (Ber. 1907, 40, 4336). Methyl ethyl ketone (850 c.c.) is converted into the *iso*nitroso derivative (diacetyl monoxime) by amyl nitrite (1 litre) and hydrochloric acid (30 c.c., sp.gr. 1·19). The oxime is extracted with dilute sodium hydroxide solution; after acidifying the diacetyl is blown over in a current of steam and the ketone eventually separated from water. 4 kilos of methyl ethyl ketone give 1300 grams of diacetyl; b.p. 87°–88°.

Diacetyl has also been obtained by the oxidation of acetylmethylcarbinol, a product of growth of certain bacteria on sugars (Harden and Norris, J. Physiol. 1911, 42, 332), and by the action of hydrochloric acid on α-triazomethylaceto-acetic ester (Forster and Newman, Chem. Soc. Trans. 1910, 97, 1360.)

The dimeric form of diacetyl discovered by von Pechmann probably possesses the structure



$$C(CH_3)(OH){<}\begin{array}{l} CO{\cdot}CH_2 \\ CH_2{\cdot}CO \end{array}{>}C(CH_3)(OH)$$

(Diels, Blanchard and von der Heyden, Ber. 1914, 47, 2355).

Diacetyldioxime (dimethylglyoxime)

$$CH_3{\cdot}C(:NOH)C(:NOH)CH_3$$

has acquired importance as a reagent for nickel. The solution to be tested is treated with an excess of ammonia or sodium acetate and then a little dimethylglyoxime is added and the solution boiled. If nickel is present a scarlet precipitate is produced. Definite results may be obtained with solutions containing 1 part of nickel in 400,000 of water. When cobalt is present, the solution is first shaken with a large excess of ammonia, 0·1 mg. of nickel can be detected in the presence of 500 mg. of cobalt (L. Tschugaeff, Ber. 1905, 38, 2520).

Convenient methods for the preparation of dimethylglyoxime have been given by Tschugaeff (*l.c.*), A. Gandarin (J. pr. Chem. 1908, [ii.] 77, 414), and H. Biltz (Zeitsch. anal. Chem. 1909, 48, 164). Biltz's method consists in passing gaseous hydrogen chloride through a well-cooled solution of 50 grams of methyl ethyl ketone in 100 grams of ether, 82 grams of amyl nitrite being added drop by drop. After a few hours the monoxime is extracted by caustic soda solution (150 c.c. iced water and 50 c.c. 33 p.c. caustic soda), the ethereal layer extracted a few times with dilute caustic soda, the alkaline solutions united, extracted with a little ether and somewhat evaporated. After cooling, the solution is carefully neutralised with dilute sulphuric acid, and 50 grams of hydroxylamine hydrochloride dissolved in 75 c.c. of water are added. The dioxime crystallises out on standing over-night, and is purified by recrystallisation. The yield amounts to 45–50 grams (*v.* Dimethylglyoxime).

On oxidising the monohydrazone of diacetyl, azibutanone $CH_3{\cdot}CO{\cdot}C(N_2){\cdot}CH_3$ is produced. It is a mobile deep orange liquid giving an olive-green vapour; b.p. 45°/12mm. (Diels and Pflaumer, Ber. 1915, 48, 223)

Hydrazoxime $CH_3{\cdot}C(:NOH){\cdot}C(:N_2H_2){\cdot}CH_3$, m.p. 140° (Forster and Dean, Chem. Soc. Trans. 1912, 101, 2238

Hexabromo-diacetyl, m.p. 100°–101° (Jackson and Adams, J. Amer. Chem. Soc. 1915, 37, 2322).

Benzil $C_6H_5{\cdot}CO{\cdot}CO{\cdot}C_6H_5$ is obtained by the oxidation of benzoin $C_6H_5{\cdot}CO{\cdot}CH(OH)C_6H_5$, which may be prepared by heating for a short time 200 grams of pure benzaldehyde with 20 grams of potassium cyanide dissolved in 800 grams of 50 p.c. alcohol under reflux. The solution is allowed to cool, benzoin separates, and is collected, the filtrate yields a further quantity of benzoin when heated with more potassium cyanide (Zincke, Annalen, 1879, 198, 151). The benzoin is then heated with twice its weight of nitric acid (sp.gr. 1·4) until red fumes are no longer evolved, the whole is poured into water, and the benzil, which then solidifies, purified by crystallisation from alcohol (Zinin, Annalen, 1840, 34, 188).

Benzil crystallises in six-sided prisms; m.p. 95°; b.p. 346°–348° (corr. with slight decomposition). Easily soluble in alcohol and ether. Is reduced to benzoin by iron and acetic acid, or zinc and hydrochloric acid (Zinin, Annalen, 1[illegible], 119, 177) and to hydrobenzoin

$$C_6H_5{\cdot}CH(OH)CH(OH)C_6H_5$$

by sodium amalgam (Zincke and Forst, Ber. 1875, 8, 797). Other reactions have already been mentioned under 1 : 2-diketones.

Ammonia, in presence of air, forms several compounds. If air is excluded, triphenyloxazole and ammonium benzoate are produced almost quantitatively (Schönberg, Ber. 1921, 54, 242). The condensation of benzil with benzidine has been studied by Cain and Micklethwaite (Trans. Chem. Soc. 1914, 105, 1437) and Ferriss and Turner (Trans. Chem. Soc. 1920, 117, 1140).

Benzil yields substitution products with difficulty, it may be nitrated by boiling with fuming nitric acid. Two dinitrobenzils (m.p.'s 131° and 147°) are produced; these may be mechanically separated as crystals. The mixture of dinitrobenzils can be reduced, the resulting diamino-compound (? a mixture), though not isolated, can be used as a component in the preparation of azo dyestuffs (Poirrier and Rosenstiehl, D. R. PP. 44269 and 45789).

Four di-oximes of benzil have been described, these are known as α, β, γ and δ modifications. δ-Benzil dioxime may be used for the estimation of nickel (Atack, Analyst, 1913, 38, 317).

OPEN CHAIN TRI- AND TETRA-KETONES.

Triketones. *Preparation.*—(1) F. Sachs and H. Barschall (Ber. 1901, 34, 3047) obtained triketopentane by condensation of nitrosodimethylaniline with acetylacetone and hydrolysis of the resulting azomethine compound :

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_3+ON{\cdot}C_6H_4{\cdot}N(CH_3)_2$$
$$=H_2O+CH_3{\cdot}CO{\cdot}C[:N{\cdot}C_6H_4N(CH_3)_2]CO{\cdot}CH_3$$
$$CH_3{\cdot}CO{\cdot}C[:N{\cdot}C_6H_4N(CH_3)_2]CO{\cdot}CH_3+H_2O$$
$$=H_2N{\cdot}C_6H_4{\cdot}N(CH_3)_2+CH_3{\cdot}CO{\cdot}CO{\cdot}CO{\cdot}CH_3$$

(Later papers by Sachs, Ber. 1902, 35, 3307 ; 1903, 36, 3221 ; 1907, 40, 2714.)

Diphenyltriketone $C_6H_5{\cdot}CO{\cdot}CO{\cdot}CO{\cdot}C_6H_5$ has been described by Gastaldi and Cherchi (Gazz. chim. ital. 1913, 43. i. 299).

(2) Aromatic triketones with open chain have been obtained by Wieland and Bloch (Ber. 1904, 37, 1524). By the action of nitrous gases evolved from a mixture of arsenious oxide and nitric acid (sp.gr. 1·38) on an ethereal solution of dibenzoylmethane, the bisnitroso derivative of the latter compound and diphenyltriketone are obtained. The latter crystallises with water, probably of constitution ; in fact the colourless hydrates give coloured triketones by loss of water. The same behaviour is observed in the case of cyclic triketones ; Ruhemann (Chem. Soc. Trans. 1910, 2025 ; 1911, 792, 1306, 1486) finds that the coloured triketohydrindene not only forms a colourless monohydrate, but also gives colourless addition products with guanidine, benzamidine, and hydrogen cyanide.

Branched triketones have been described. For the supposed stereoisomerism of dibenzoylacetylmethane, *see* Michael (Ber. 1906, 39, 203 ; Annalen, 1912, 390, 40) and Dieckmann (Ber. 1916, 49, 2203).

Tetraketones are also known.

2 : 4 : 5 : 7-*Octanetetrone*

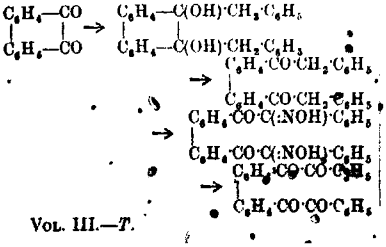
$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_3$$

is obtained by adding sodium ethoxide (free from alcohol) to an ethereal solution of acetone and diethyl oxalate (Claisen and Stylos, Ber. 1888, 21, 1142). With acetophenone, &c., corresponding aromatic compounds can be prepared.

o-o′-**Dibenzil**

$$C_6H_5{\cdot}CO{\cdot}CO{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}CO{\cdot}CO{\cdot}C_6H_5$$

has been obtained by Zincke and Tropp (Annalen, 1908, 363, 302). Phenanthraquinone is treated with magnesium benzyl halide, the resulting di-tertiary alcohol oxidised to dibenzyldiphenylene diketone, the latter converted into a diisonitroso compound and hydrolysed :



$$\begin{array}{l}C_6H_4{-}CO\\ |\qquad\ \ |\\ C_6H_4{-}CO\end{array}\rightarrow\begin{array}{l}C_6H_4{-}C(OH){\cdot}CH_2{\cdot}C_6H_5\\ |\qquad\ \ |\\ C_6H_4{-}C(OH){\cdot}CH_2{\cdot}C_6H_5\end{array}\rightarrow\begin{array}{l}C_6H_4{\cdot}CO{\cdot}CH_2{\cdot}C_6H_5\\ |\\ C_6H_4{\cdot}CO{\cdot}CH_2{\cdot}C_6H_5\end{array}$$
$$\rightarrow\begin{array}{l}C_6H_4{\cdot}CO{\cdot}C(:NOH){\cdot}C_6H_5\\ |\\ C_6H_4{\cdot}CO{\cdot}C(:NOH){\cdot}C_6H_5\end{array}\rightarrow\begin{array}{l}C_6H_4{\cdot}CO{\cdot}CO{\cdot}C_6H_5\\ |\\ C_6H_4{\cdot}CO{\cdot}CO{\cdot}C_6H_5\end{array}$$

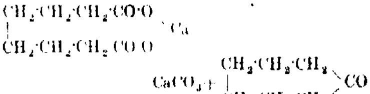
Possessing two 1 : 2-diketo- groups, the compound condenses with 2 molecules of *o*-phenylenediamine to form the corresponding *di*quinoxaline.

CYCLIC KETONES.

In the cyclic ketones the carbonyl groups form members of a closed ring ; the properties are very similar to those of the aliphatic ketones as a rule, but in the case of the ortho- and para-quinones, such special characteristics are exhibited that they will be treated in a separate article (*q.v.*).

Preparation.—The cyclic ketones may frequently be prepared by the general methods already given ; the following syntheses, or special methods, resulting in the formation of closed chain ketones, may be mentioned.

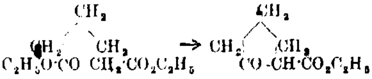
(1) The distillation of the calcium salts of certain dibasic acids gives cyclic ketones. The earliest example is the preparation of suberone from calcium suberate :



$$\begin{array}{l}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}O\\ |\\ CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}O\end{array}\!\!>Ca = CaCO_3+\begin{array}{l}CH_2{\cdot}CH_2{\cdot}CH_2\\ |\\ CH_2{\cdot}CH_2{\cdot}CH_2\end{array}\!\!>CO$$

(Boussingault, Annalen, 1836, 19, 308 ; Tilley, *ibid.* 1841, 39, 166 ; Dale and Schorlemmer, *ibid.* 1879, 199, 147). *Cyclo*pentanone, *cyclo*hexanone, and *cyclo*octanone can be obtained by similar methods from the calcium salts of adipic, pimelic, and azelaic acids (Wislicenus, Annalen, 1893, 275, 312, 364 ; v. Baeyer, *ibid.* 1875, 178, 112 ; Ber. 1893, 26, 229).

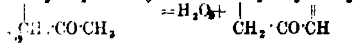
(2) The esters of certain dicarboxylic acids undergo intramolecular condensation when acted on by sodium :



(Dieckmann, Ber. 1894, 27, 102).

(3) *Cyclo*hexanone and its derivatives may be obtained by the reduction of phenols. When phenol vapour mixed with an excess of hydrogen is passed over reduced nickel at 215°–230°, *cyclo*hexanol and *cyclo*hexanone are obtained. The mixed product may be entirely converted into the latter compound by passing the vapour over copper heated to 330° (Sabatier and Senderens, Compt. rend. 1904, 137, 1025 ; 138, 457, 1257).

(4) 3-Methyl-Δ^2-*cyclo*hexenone is a product of the interaction of ethyl sodioacetoacetate and methylene iodide. Apparently the first formed 2 : 6-heptanedione undergoes intramolecular condensation :



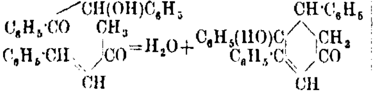
$$\begin{array}{l}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_3\\ |\\ CH_2{\cdot}CO{\cdot}CH_3\end{array}=H_2O+\begin{array}{l}CH_2{\cdot}CH_2{\cdot}C{\cdot}CH_3\\ |\qquad\qquad\ \ \|\\ CH_2{\cdot}CO{\cdot}CH\end{array}$$

(C. J. L. Hagemann, Ber. 1893, 26, 876).

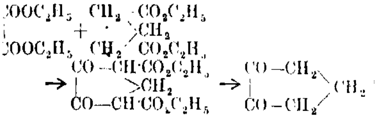
*iso*Butylidene diacetoacetic ester undergoes a similar internal condensation, giving an ester from which 3-methyl-5-*iso*propyl-Δ^2-*cyclo*-hexenone may be obtained (Knoevenagel, Annalen, 1896, 289, 131).

(5) Open chain ketones will condense with unsaturated aldehydes or unsaturated ketones

f the type of benzalacetone. Thus the latter ompound, condensed with benzoïn, gives 1 : 4 : 5-triphenyl-4-hydroxy-Δ^2-*cyclo*hexenone (Garner, Amer. Chem. J. 1904, 31, 143):

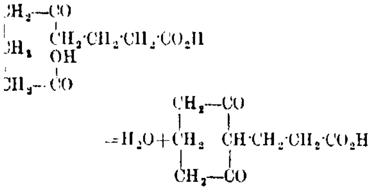


(6) Cyclic 1 : 2-diketones may be obtained y the condensation of diethyl glutarate and its derivatives with diethyl oxalate in presence of odium ethoxide:

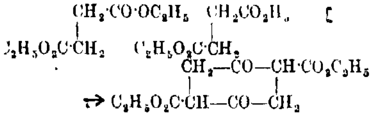


Dieckmann, Ber. 1897, 30, 1470; 1899, 32, 933; *cf.* papers by W. H. Perkin, jun., and o-workers, Chem. Soc. Trans. 1906, 89, 1640; 908, 93, 1943; 1909, 95, 2010).

(7) A derivative of *cyclo*hexane-1 : 3-dione is btained by dehydration of acetonedipropionic acid (v. Pechmann and Sidgwick, Ber. 1904, 37, 3816):



(8) Two molecules of diethyl succinate are ondensed by Claisen's reaction (Herrmann, nnalen, 1882, 211, 311):

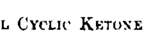


The resulting ester yields *cyclo*hexanedione (*vide infra*).

Individual Cyclic Ketones.

I. *Monocyclic Monoketones.*

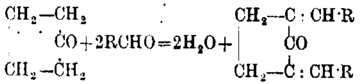
***cyclo*Pentanone**



$CH_2<\begin{matrix}CH_2\cdot CO\\ CH_2\cdot CH_2\end{matrix}$

occurs in raw wood spirit, and may be obtained by the distillation of calcium adipate (J. Wislicenus and Hentzschel, Annalen, 1893, 275, 312, 318; *cf.* Bayer & Co., D. R. P. 256622). The oil of wood spirit is distilled, and the fraction boiling at 120°–140° shaken with syrupy sodium bisulphite. The resulting crystalline bisulphite compound is well pressed, decomposed with warm saturated sodium carbonate solution, and the oil freed from pyridine bases by shaking with a saturated solution of oxalic acid. The compound obtained is identical with the 'Dumasin' obtained by Kane from acetone oil (J. pr. Chem. 1838, 13, 69).

Mobile oil smelling like peppermint; b.p. 130°–130·5°; sp.gr. 0·9416 at 21·5°/4°. *Oxime* $C_5H_8:NOH$, m.p. 56·5°; b.p. 196°. Condenses with 2 molecules of aromatic aldehydes in presence of alkalis (Vorländer and Hobohm, Ber. 1896, 29, 1836):

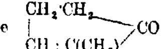


Since the resulting compounds crystallise well, and ketones and aliphatic aldeyhdes do not react with *cyclo*pentanone, Mentzel recommends the reaction for the recognition of aromatic aldehydes (Ber. 1903, 36, 1499). Vorländer and Hobohm have shown that the 'pyroxanthin' obtained by Scanlan, Apjohn and Gregory (Annalen, 1837, 21, 143), by the action of alkalis on raw wood spirit is difuralcyclopentanone.

Hydrogenation of *cyclo*pentanone in presence of reduced nickel at 125° yields *cyclo*pentane, *cyclo*pentanol (50 p.c.) and a ketone $C_{10}H_{16}O$, which is probably α-*cyclo*pentyl*cyclo*pentanone (Godchot and Taboury, Compt. rend. 1911, 152, 881).

Numerous derivatives of *cyclo*pentanone have been described (Perkin and co-workers, Chem. Soc. Trans. 1906, 89, 1641; 1908, 93, 573; 1912, 101, 405; Dieckmann, Ber. 1894, 27, 102, 965; Ruhemann, Chem. Soc. Trans. 1912, 101, 1729, 2542; Stobbe, J. pr. Chem. 1912, ii. 86, 209; 1914, ii. 89, 329; Godchot and Taboury, Compt. rend. 1911, 153, 1060; 1912, 155, 1522; 1913, 156, 332; Haller and Cornubert, Compt. rend. 1914, 158, 1616, 1739; Bauer, Ann. Chim. 1914, [ix] 1, 393).

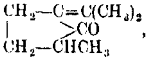
Unsaturated ketones containing 5-carbon rings are known. Methyl*cyclo*pentenolone $C_6H_8O_2$, m.p. 106°, b.p. 200°, occurs in wood vinegar (Meyerfeld, Chem. Zeit. 1912, 36, 549). Methyl*cyclo*pentenone



$\begin{matrix}CH_2\cdot CH_2\\ |\\ CH:C(CH_3)\end{matrix}>CO$

, b.p. 157°, found in wood oils, has been identified with synthesised material (Godchot, Compt. rend. 1914, 158, 506).

Camphophorone

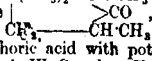


$\begin{matrix}CH_2-C=C(CH_3)_2\\ |\qquad >CO\\ CH_2-CHCH_3\end{matrix}$

, first obtained by Gerhardt and Lies-Bodart (Annalen, 1849, 72, 293) by distillation of calcium camphorate, smells like peppermint; b.p. 200°–205° sp.gr. 0·9305 at 20°/4°.

Pulegenone is isomeric with camphophorone, both compounds give 2-methyl-5-*iso*propyl*cyclo*pentanone (dihydrocamphorone, dihydropulegenone) on reduction. *Dihydrocamphorone*, b.p. 184°–185°; *oxime*, m.p. 77°–78°; *semicarbazone*, m.p. 193°–195° (Semmler, Ber. 1902, 35, 1022; Wallach, Annalen, 1903, 327, 125). For conversion of menthone into pulegenone *v.* Wallach and Grote, Chem. Zentr. 1918, ii. 120; Abst. Chem. Soc. 1918, i. 544.

Dihydrocamphoketone



$\begin{matrix}C(CH_3)_2-CH\cdot CH_3\\ |\qquad >CO\\ CH_2-CH\cdot CH_2\end{matrix}$

, results on fusion of camphoric acid with potash (W. H. Perkin, jun., and A. W. Crossley, Chem. Soc. Trans. 1898, 73, 26). Smells like peppermint, b.p. 180°–181°; *semicarbazone*

$C_9H_{16}:N\cdot NH\cdot CO\cdot NH_2$

m.p. 202°–203°.

***cyclo*Hexanone** $\begin{array}{l}CH_2\cdot CH_2\cdot CO\\ CH_2\cdot CH_2\cdot CH_2\end{array}$ occurs with other cyclic ketones in wood oil (Looft, Ber. 1894, 27, 1544); it may be obtained by distillation of calcium pimelate (*v.s.*); by the oxidation of synthetic *cyclo*hexanol (v. Bayer, Ber. 1893, 26, 229; Annalen, 1894, 278, 88); or by the reduction of phenol by alternate current (Drechsel, J. pr. Chem. 1888, [ii.] 38, 65); or by reduction in presence of nickel (*v.s.*), the last method being used technically.

*Cyclo*hexanone is obtained in 97 p.c. yield when a solution of nitro*cyclo*hexane in caustic potash is oxidised by permanganate (Nametkin and Pozdujakova, J. Russ. Phys. Chem. Soc. 1913, 45, 1420).

Mobile oil, somewhat soluble in water, smells like peppermint; b.p. 155·4°; sp. gr. 0·9471 at 22°/4°. Gives a bisulphite compound; condenses with 2 molecules of benzaldehyde (Vorländer and Hobohm, Ber. 1896, 29, 1840); yields a di*iso*nitroso derivative (W. Borsche, Festschrift Otto Wallach, 1909, 31).

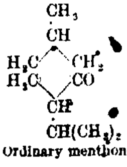
Oxime $C_6H_{10}:NOH$, m.p. 88°; *phenylhydrazone* $C_6H_{10}:N\cdot NH\cdot C_6H_5$, m.p. 74°–77° (Kötz and Grethe, J. pr. Chem. 1909, ii. 80, 473).

A very large number of derivations of cyclopentanone have been prepared. (Bodroux, Cornubert, Crossley, Darzens, Favorski, Guareschi, Haller, Kijner, Kötz, Leser, Perkin, Saytzeff, Squintani, Stobbe, Wallach, &c.)

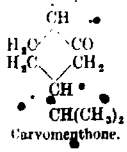
4-Methyl*cyclo*hexanone $\begin{array}{l}CH_2\cdot CH_2\cdot CO\\ |\qquad\qquad |\\ C(CH_3)CH_2\cdot CH_2\end{array}$ is obtained by the oxidation of 4-methyl*cyclo*hexanol with nitric acid. Oxidation of methylcyclohexanone with alkaline permanganate gives β-methyladipic acid, a compound which finds employment in the manufacture of dyes and pharmaceutical products (Farbenf vorm. Fr. Bayer & Co., D. R. P. 221849).

Menthanones $C_{10}H_{18}O$. Ordinary menthone was first obtained in an inactive form by Moriya (Chem. Soc. Trans. 1881, 39, 77) by the oxidation of natural menthol; Atkinson and Yoshida obtained a strongly dextro-rotatory variety (*ibid.* 1882, 41, 50). Beckmann has examined the stereochemistry of the menthones at length (Annalen, 1889, 250, 325; 1896, 289, 362; J. pr. Chem. 1897, [ii.] 55, 14). Other derivatives (Bödtker, Compt. rend. 1912, 154, 437).

Carvomenthone (tetrahydrocarvone) was discovered nearly simultaneously by v. Baeyer (Ber. 1893, 26, 822; 1895, 28, 1588; 1896, 29, 27) and Wallach (Annalen, 1893, 277, 133; 1895, 286, 102; 1899, 305, 266; 1900, 312, 302; Ber. 1895, 28, 1961). Ordinary menthone and carvomenthone can each exist in four stereoisomeric forms, their structures are given by



Ordinary menthone.



Carvomenthone.

The reactions of the methylene group adjacent to carbonyl in menthone and tanacetone have been studied by Cusmano (Gazzetta, 1919, 49, i. 26), and the electrolytic reduction of menthone by Matsui and Shimizu (Mem. Coll. Sci. Kyoto, 1920, 4, 245).

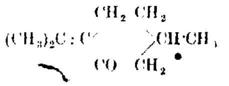
Δ²-*cyclo*Hexenone C_6H_8O has been obtained from *cyclo*hexanone (A. Kötz and T. Grethe, J. pr. Chem. 1909, [ii.] 80, 473).

The characteristic smell of urine has been attributed to a substance, *urinod*, b.p. 108°/28 mm. This compound occurs in a conjugated state in urine, it is probably *cyclo*hexene-4-one (Dehn and Hartmann, J. Amer. Chem. Soc. 1914, 36, 2136).

Methyl*cyclo*hexenone $CH_3\cdot C_6H_7O$. In addition to the compound synthesised from ethyl sodioacetoacetate by methylene iodide (Hagemann, Ber. 1893, 26, 876), and formaldehyde (Knoevenagel, *ibid.* 1090), an isomeride (m.p. 12°, b.p. 192°) has been discovered in wood tar. Since this gives acetic and lævulic acids on oxidation with potassium permanganate the constitution $\begin{array}{l}CH\cdot CH_2\cdot CO\\ \qquad\quad\ |\\ CH_3\cdot C\cdot CH_2\cdot CH_2\end{array}$ has been deduced (Béhal, Compt. rend. 1897, 125, 1036; 1901, 132, 342)

***iso*Camphor** $\begin{array}{l}CH_2\quad CH_2-CO\\ |\qquad\qquad\quad |\\ CH(C_3H_7)\cdot CH:C\cdot CH_3\end{array}$ was obtained by Angeli and Rimini by acting on camphoroxime with nitrous acid and decomposing the resultant nitrimine with ice-cold sulphuric acid (Gazz. chim. ital. 1898, ii. 26, 34).

Pulegone (Δ^{1(8)}-3-menthenone)



$$(CH_3)_2C:C<\begin{array}{l}CH_2\cdot CH_2\\ CO\cdot CH_2\end{array}>CH\cdot CH_3$$

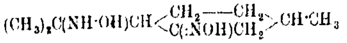
is the most important of the seven possible structurally different *p*-menthenones. (Each of these exhibits stereoisomerism.) Beckmann and Pleissner (Annalen, 1891, 262, 1) obtained pulegone from oil of pennyroyal (*Mentha Pulegium* [Linn.]) of which it constitutes about 80 p.c. It is also found in the ethereal oils of *Hedeoma pulegioides* (Pers.) and *Pycnanthemum lanceolatum* (Pursh.). It is isolated from oil of pennyroyal by fractional distillation and conversion into the sodium bisulphite derivative. The synthesis from citronellal has been effected by Tiemann and Schmidt (Ber. 1897, 30, 22); b.p. 221°–222°; sp.gr. 0·936; $[\alpha]_D+22\cdot89°$.

The crystalline hydrochloride $C_{10}H_{17}OCl$ (m.p. 24°–25°) and hydrobromide $C_{10}H_{17}OBr$ (m.p. 40·5°) give pulegone on treatment with alcoholic potash.

Semicarbazone $C_{10}H_{16}:N\cdot NH\cdot CO\cdot NH_2$, m.p. 172°; *oxime* $C_{10}H_{16}:NOH$, m.p. 118°–119°. Addition of hydroxylamine at the double linkage gives 8-*hydroxylaminomenthone*

$$(CH_3)_2C(NH\cdot OH)\cdot CH<\begin{array}{l}CH_2\cdot CH_2\\ CO\cdot CH_2\end{array}>CH\cdot CH_3$$

(m.p. 157°, $[\alpha]_D-83\cdot44°$) which may be successively oxidised to 8-*nitrosomenthone* (chromic acid) and 8-*nitromenthone*, m.p. 60° (nitric acid, sp.gr. 1·16) (Harries and Roeder, Ber. 1899, 32, 3364). The so-called pulegone dioxime, m.p. 118°, has the constitution



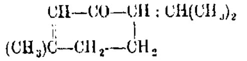
$$\mathrm{(CH_3)_2C(NH{\cdot}OH)CH}{<}\begin{matrix}\mathrm{CH_2\text{——}CH_2}\\\mathrm{C(:NOH)CH_2}\end{matrix}{>}\mathrm{CH{\cdot}CH_3}$$

(Semmler, Ber. 1905, 38, 147).

On reduction, the following products are obtained, viz.: pulegol (Tiemann and Schmidt, Ber. 1896, 29, 914); menthol (Beckmann and Pleissner, Annalen, 1891, 262, 30); and a bimolecular reduction product, m.p. 119°, probably the corresponding pinacone (Harries and Roeder, Ber. 1899, 32, 3367; Law, Chem. Soc. Trans. 1912, 101, 1029; Paolini, Atti R. Accad. Lincei, 1919, [v.] 28, ii. 190).

For the identification of pennyroyal, v. Baeyer and Henrich recommend conversion into the *bis*nitroso compound $(C_{10}H_{15}O_2N)_2$. 2 c.c. pulegone, 2 c.c. petroleum spirit, and 1 c.c. amyl nitrite are mixed, and very little concentrated hydrochloric acid added; the mixture becomes milky in 20–25 seconds, and solidifies to a paste of fine long needles of the nitroso compound. This compound cannot be recrystallised, it dissolves in cold ammonia with a yellow colour (Ber. 1895, 28, 654).

Δ′-3-Menthenone



$$\begin{array}{l}\qquad\mathrm{CH{-}CO{-}CH:CH(CH_3)_2}\\\qquad\ \|\qquad\qquad\ |\\\mathrm{(CH_3)C{-}CH_2{-}CH_2}\end{array}$$

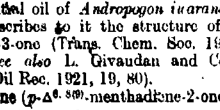
prepared by Wallach and Meister (Annalen, 1908, 362, 261) from 1 : 3 : 4-trihydrxoyterpane has been identified as a constituent of Japanese peppermint oil (Schimmel's Bericht, October, 1910), b.p. 235°–237°. *Oxime*, m.p. 107°–109°; *oxaminooxime*, m.p. 164°–165°; two *semicarbazones*, α, m.p. 224°–226°; β, m.p. 171°–172°.

Piperitone $C_{10}H_{16}O$ occurs in *Eucalyptus piperita*. The green leaves and twigs of *E dives* yield about 4 per cent. of the oil which contains up to 40 per cent. of piperitone (J. Proc. Roy. Soc. N.S. Wales, 1900, 34, 316). Smith and Penfold (*ibid.* 1620, 54, 40) have shown that it is an unsaturated lævo-rotatory ketone which racemises on distillation under ordinary pressure. The maximum observed value of $[\alpha]_D$ was $-42{\cdot}8°$; this specimen gave d_4^{20} 0·9348; n_D^{20} 1·4837; R_L 46·49; b.p. 106°–107°/10 mm., 229°–230°/760 mm. Practically the same values are given by the optically inactive substance.

Several derivatives of the *dl*-form have been described by J. Read and H. G. Smith (Trans. Chem. Soc. 1921, 119, 779). On oxidation with ferric chloride and acetic acid, thymol is produced, whilst Smith and Penfold obtained menthone on reduction with hydrogen in presence of a nickel catalyst.

d-Piperitone has been found by Simonsen in the essential oil of *Andropogon iwarancusa*, the author ascribes to it the structure of *d*-Δ¹-*p*-menthen-3-one (Trans. Chem. Soc. 1921, 119, 1644. *See also* L. Givaudan and Co., *Perf.* Essent. Oil Rec. 1921, 19, 80).

Carvone (*p*-Δ⁶· ⁸⁽⁹⁾-menthadiene-2-one)



occurs naturally in dextro- and lævo-rotatory forms. The former (b.p. 224°, sp.gr. 0·9598 at 20°/4° $[\alpha]_D$ +62·07°) occurs in the oils of carraway (*Carum Carvi* [Linn.]), fennel (*Fœniculum vulgare* (Mill.), and dill (*Peucedanum graveolens* [Benth. et Hook.]). The lævo-rotatory form (b.p. 223°–224°; sp.gr. 0·9593 at 20°/4°; $[\alpha]_D$ −62·41°) occurs in spear mint (*Mentha viridis* [Linn.]) and kuromoji (*Lindera sericea* [Blume]). The isolation of carvone from oils is effected by conversion into the compound with hydrogen sulphide $(C_{10}H_{14}O)_2H_2S$, and subsequent decomposition with alcoholic potash. When heated, carvone yields carvacrol $C_6H_3(OH)(CH_3)(i\text{-}C_3H_7)$. The isomerisation to carvacrol by heating with hydrochloric acid (D. 1·19) at 120°–125° is said to involve the intermediate formation of 8-chloro-Δ⁶-menthene-2-one (Arno Müller, J. pr. Chem. 1916, ii. 93, 10). The active *carvoximes* melt at 72°, the inactive at 93°. Carvoxime was first obtained by Tilden by the action of alcoholic potash on limonene nitrosochloride (J. 1877, 428). *d*-α- and *d*-β-Limonene nitrosochlorides correspond to *l*-carvone, the *l*α- and *l*β-nitrosochlorides to *d*-carvone, whilst α- and β-dipentene nitrosochlorides give the oxime of *r*-carvone (Wallach, Annalen, 1888, 245, 256; 246, 226; 1891, 270, 171).

Harries has described a method for preparation of the carvoximes (Meyer-Jacobson's Lehrbuch, 1902, II. 939).

Hydrochlorocarvoxime $C_{10}H_{15}Cl : NOH$ melts at 135° (*d*- or *l*-) or 125·5° (*r*-). The melting-points of the *hydrobromocarvoximes*

$$C_{10}H_{15}Br : NOH$$

are 133°–134° (*d*- or *l*-) and 128°–129° (*r*-).

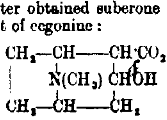
d-Carvone yields *m*- and *p*-nitrophenylhydrazones $C_{10}H_{14} : N{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2$, which melt at 105°–106° and 174°–175° respectively (W. Borsche, Annalen, 1908, 359, 49).

Carvelone $C_{20}H_{30}O_2$ is obtained on reduction (Harries, Ber. 1899, 32, 1316). A second carvelone is known (Law, Chem. Soc. Trans. 1912, 101, 1028). Dihydrocarvone is produced on electrolytic reduction in aqueous alcoholic solution, using a copper cathode (Law, *ibid.* 1549).

Suberone $C_7H_{12}O$ (Preparation, General Method 1), smells like peppermint; b.p. (742 mm.) 178·5° sp.gr. 0·9685 at 0°.

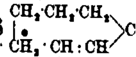
Oxime $C_7H_{12} : NOH$, m.p. 23·3°, b.p. 230°; *semicarbazone* $C_7H_{12} : N{\cdot}HN{\cdot}CO{\cdot}NH_2$, m.p. 163°; *dibenzal derivative* $C_7H_8O(:CH{\cdot}C_6H_5)_2$, m.p. 107°–108°; *sulphonal* $C_7H_{12}(SO_2C_2H_5)_2$ (by the action of mercaptan in presence of hydrogen chloride and oxidation of the resultant mercaptol), m.p. 136°–139°. Suberone gives ζ-hydroxyœnanthoic acid by oxidation with Caro's acid (v. Baeyer, Ber. 1900, 33, 962). Further derivatives are described by Tarbouriech (Compt. rend. 1913, 156, 75).

Willstätter obtained suberone as a degradation product of ecgonine:



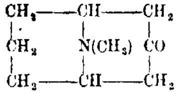
$$\begin{array}{lll}\mathrm{CH_2{-}CH} & \text{——} & \mathrm{CH{\cdot}CO_2H}\\ | & \mathrm{N(CH_3)} & \mathrm{CHOH}\\\mathrm{CH_2{-}CH} & \text{——} & \mathrm{CH_2}\end{array}$$

(Ber. 1898, 31, 2498). Tropinone and *r*-ecgonine have been completely synthesised by Willstätter and Bommer (Annalen, 1921, 422, 15).

Tropilene , an oil of high refractive power and odour of bitter almonds, is difficultly soluble in water, and boils at 180°–188°. It is obtained from tropine by exhaustive methylation (Ladenburg, Ber. 1881, 14, 2403; Annalen, 1883, 217, 132, 138; Merling, Ber. 1891, 24, 3123); its constitution was correctly recognised by Willstätter (Ber. 1898, 31, 1545; 1901, 34, 133).

*cyclo***Octanone** $C_8H_{14}O$ was obtained by Mager (Annalen, 1893, 275, 363) by distilling the calcium salt of azelaïc acid, b.p. about 205°.

*pseudo***Pelletierine** or *methylgranatonine* is an alkaloid obtained from the pomegranate tree (*Punica Granatum* [Linn.]). Its constitution has been determined as:



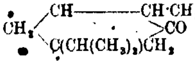
by Willstätter and Veraguth (Ber. 1905, 38, 1975, 1984).

II. *Bicyclic Monoketones.*

Of the numerous monoketones derived from bicyclic hydrocarbons only a few can be mentioned.

Thujone (Tanacetone) $C_{10}H_{16}O$ is known in stereoisomeric forms, it occurs in *Arbor vitæ* (*Thuja occidentalis* [Linn.]), tansy (*Tanacetum vulgare* [Linn.]), *Artemisia* and *Salvia*. α-Thujone predominates in thuja oil, $[\alpha]_D -10{\cdot}23°$; *oxime* $C_{10}H_{16}:NOH$, $[\alpha]_D -25{\cdot}25°$ in ethereal solution, *semicarbazone* $C_{10}H_{16}:N{\cdot}NH{\cdot}CO{\cdot}NH_2$ $[\alpha]_D +59{\cdot}9°$ in methyl alcoholic solution. β-Thujone is found in tansy oil $[\alpha]_D$ about +70°, *oxime*, m.p. 54°–55°, $[\alpha]_D +105{\cdot}1°$ in methyl alcoholic solution; *semicarbazone*, dimorphic, hexagonal, m.p. 174°–175°, rhombic, m.p. 170°–172°. Other derivatives *v.* Kijner, J. Russ. Phys. Chem. Soc. 1910, 42, 1198; 1911, 43, 577, 951, 1132.

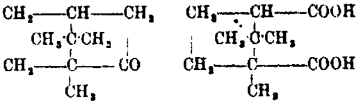
Artemisia oil seems to contain a third feebly dextro-rotatory thujone (Wallach, Annalen, 1893, 275, 179; 1894, 279, 383; 1895, 286, 90; 1904, 336, 247). Thujone probably possesses the structure:



(Tschugaeff, Ber. 1900, 33, 3122; Semmler, *ibid.* 1900, 33, 275; 1903, 36, 4367; D. Thomson, Chem. Soc. Trans. 1910, 97, 1502).

Carone $C_{10}H_{16}O$, obtained by the action of alcoholic potash on the hydrobromide of dihydrocarvone, is also probably bicyclic (v. Baeyer, Ber. 1894, 27, 2715; 1895, 28, 639, 1586; 1896, 29, 3, 2796; 1898, 31, 1401, 2067).

Camphor $C_{10}H_{16}O$ (*q.v.*) occurs in the dextro-rotatory form ($[\alpha]_D +44{\cdot}22°$ in 20 p.c. alcoholic solution) in *Cinnamomum Camphora* (Nees and Eberm.) and other plants, m.p. 178·4°, b.p. 209°. The lævo- forms occurs in the oils of *Matricaria*, *Salvia*, and *Tanacetum*. Bredt gives the following formulæ for camphor and its oxidation product, camphoric acid (Ber. 1893, 26, 3047; Annalen, 1896, 292, 55):—

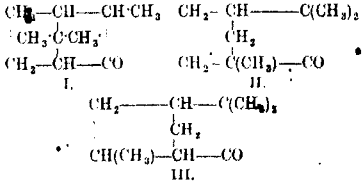


Camphor has been obtained by distillation of the lead (Haller) and calcium (Bredt and Rosenberg) salts of homo- camphoric acid: respecting the synthesis of camphoric acid, *see* Kommpa (Ber. 1903, 36, 4332), Blanc and Thorpe (Chem. Soc. Trans. 1910, 97, 836), and Kommpa (Chem. Soc. Trans. 1911, 99, 29).

In *Epicamphor* $[\alpha]_D -58{\cdot}2°$, m.p. 182°, the positions of the carbonyl and adjacent methylene group are interchanged (Lankshear and Perkin, Proc. Chem. Soc. 1911, 27, 167; Bredt and Perkin, Trans. Chem. Soc. 1913, 103, 2182; Furness and Perkin, *ibid.* 1914, 105, 2024; Perkin and Titley, *ibid.* 1921, 119, 1089).

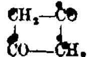
Fenchone $C_{10}H_{16}O$ occurs in nature as optical antipodes. The dextro-rotatory modification was found by Wallach and Hartmann (Annalen, 1890, 259, 324) in the portion of fennel oil boiling at 190°–195°, whilst *l*-fenchone is a constituent of the corresponding fraction of thuja oil. The two fenchones melt at 5°–6°, boil at 192°–193°; sp.gr. 0·9465 at 19°. *d*-Fenchone gives $[\alpha]_D +71{\cdot}97°$, the *l*-fenchone a slightly lower value (*see* also Bartram and Helle, J. pr. Chem. 1900, [ii.] 61, 293). Fenchone does not combine with sodium bisulphite; the *oximes* melt at 161°. Many derivatives have been prepared by Wallach; much *m*-cymene is produced on heating to 115°–130° with phosphorus pentoxide (Annalen, 1891, 263, 129; 1892, 269, 326; 1893, 272, 99; 1893, 275, 145; 1895, 284, 324; 1901, 315, 291).

Of the following formulæ for fenchone:



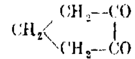
the first was proposed by Wallach, the other two by Semmler (Ber. 1906, 39, 2577). L. Bouveault and F. Levallois prefer formula II. above (Semmler's first formula), and have brought forward considerable evidence in its favour (Compt. rend. 1908, 146, 180; 1909, 148, 1399, 1524; Bull. Soc. chim. 1910, [iv.] 7, 542, 683, 736, 807, 963, 968; Wallach, Annalen, 1911, 379, 182, 215). Other bicyclic ketones are described by Godchot and Taboury (Compt. rend. 1919, 169, 1168).

III. *Monocyclic Diketones, &c.*

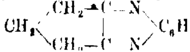
1 : 3-*cyclo***Butanedione** . This is possibly the dimeric form of ketene (Chick and Wilsmore, Chem. Soc. Trans. 1908, 93, 946;

1910,, 97, 1978). One ketone group may be enolised, in which case the substance is really Δ'-*cyclo*buten-1-ol-3-one (Staudinger and Bereza, Ber. 1909, 42, 4908). Derivatives are described Schroeter, Ber. 1916, 49, 2697).

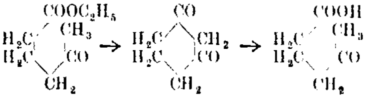
1 : 2-*cyclo***Pentanedione**



$$CH_2\left\langle\begin{array}{l}CH_2-CO\\ \qquad\quad\ |\\ CH_2-CO\end{array}\right.$$

(*preparation, v.s.*) is easily soluble in water, the solution reddens litmus, and is coloured violet by ferric chloride. In some respects it behaves as if one ·CH_2·CO· group were enolised, giving a phenylurethane $C_6H_5O·O·CO·NH·C_6H_5$, m.p. 122°, and benzoyl ester $C_5H_5O·O·CO·C_6H_5$, m.p. 72°–73°. As a 1 : 2-diketone it yields a *dioxime* $C_5H_6(:NOH)_2$, m.p. 210°; an *osazone* $C_5H_6(:N\,NH·C_6H_5)_2$, m.p. 146°; and a *quinoxaline*  $CH_2\left\langle\begin{array}{l}CH_2-C-N\\ CH_2-C\ \ N\end{array}\right\rangle C_6H_4$, m.p. 102°-103°.

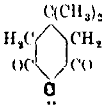
1 : 3-*cyclo***Hexanedione** (Dihydroresorcinol) $C_6H_8O_2$ was obtained by Merling by the reduction of resorcinol in boiling alcoholic solution with sodium amalgam, carbon dioxide being led in during the operation (Annalen, 1894, 278, 28). Vorlander synthesised the diketone by the action of sodium on ethyl γ-acetobutyrate (Ber. 1895, 28, 3428); barium hydroxide breaks the ring, giving γ-acetobutyric acid :



m.p. 104°-106°; *dioxime*, m.p. 154°-157°; *monophenylhydrazone*, m.p. 176°-177°. Alkyl and aryl derivatives, *see* Borsche, Ber. 1909, 42, 4496.

Dimethyldihydroresorcinol (1 : 1 dimethyl-*cyclo*-hexanedione-3 : 5) has been obtained by D. Vorländer (Annalen, 1897, 294, 253, 300; 1898, 304, 15) and A. W. Crossley (Chem. Soc. Trans. 1899, 75, 771); the latter chemist has examined it exhaustively (*see* later papers).

An *O*-acetyl derivative is known (Dieckmann and Stein, Ber. 1904, 37, 338); in presence of a small amount of sodium acetate the acetyl group enters into the ring. For the resulting *O*-acetyl derivative, Crossley and Renouf (Chem. Soc. Trans. 1912, 101, 1524) consider the structure



The tautomerism of trimethyldihydroresorcin is dealt with by Crossley and Renouf (Chem. Soc. Trans. 1911, 99, 1101; 1912, 101, 1524).

Both Vorländer and Crossley condensed ethyl sodiomalonate with mesityl oxide thus obtaining ethyl 1 : 1-dimethyl*cyclo*hexane-3 : 5-dione-2-carboxylate from which 'dimethyldihydroresorcinol' was prepared by hydrolysis and elimination of carbon dioxide. M.p. 148·5°.

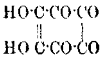
Norris and Thorpe (Trans. Chem. Soc. 1921, 119, 1199) find that *cyclo*hexenylacetone (Wallach, Annalen, 1912, 394, 362) and *cyclo*pentenylacetone (Kon, Trans. Chem. Soc. 1921, 119, 823) may also be condensed with ethyl sodiomalonate yielding esters which furnish respectively on hydrolysis and loss of carbon dioxide.

*Cyclo*hexane *spirocyclo*hexane-3 : 5-dione, m.p. 170·5° and *cyclo*pentane *spirocyclo*hexane-3 : 5-dione, m.p. 135°–136·5°. Other *spiro*-ketonic compounds, Ingold and Thorpe, (Trans Chem. Soc. 1919, 115, 320); Farmer and Ingold (Trans. Chem. Soc. 1920, 117, 1362).

1 : 4-*cyclo***Hexanedione** $C_6H_8O_2$ is obtained in small quantity by the dry distillation of calcium succinate (Feist, Ber. 1895, 28, 738). v. Baeyer (Annalen, 1894, 278, 91) obtains a good yield of the ketone in the following manner : 100 grams of diethyl diacetosuccinate are dissolved in 420 c.c. of concentrated sulphuric acid, the solution being meanwhile cooled and then poured on to ice (1450 grams). After addition of 40 c.c. of alcohol the mixture is boiled for 16 hours, the alcohol distilled off and the residue nearly neutralised with calcined sodium carbonate. The sodium sulphate is frozen out, the filtrate saturated with ammonium sulphate, and the diketone extracted with chloroform, m.p. 78°; *dioxime*, m.p. 192°; *dicyanhydrin*, m.p. 180°

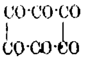
Phloroglucinol $C_6H_3(OH)_3$ 1 : 3 : 5 behaves tautomerically as *cyclo*hexanetrione, giving a *trioxime* $C_6H_6(:NOH)_3$, m.p. 155°. *See*, further, Heller, Ber. 1912, 45, 418; Goschke and Tambor, *ibid.* 1237; Sonn, Ber. 1919, 52, 255; Fuchs and Elsner, Ber. 1919, 52, 2281; 1920, 53, 886; 1921, 54, 245; Bucherer, Ber. 1920, 53, 1457; Herzig and Zeisel, *ibid.* 1518.

A few cyclic polyketones may be mentioned. The potassium carboxide $(KCO)_n$ prepared by Liebig (Annalen, 1834, 11, 182), and which forms a by-product in Brunner's method of manufacturing potassium (Brodie, Annalen, 1860, 113, 358), is the potassium derivative of hexahydroxybenzene (Nietzki and Benckiser, Ber. 1885, 18, 499; 1886, 19, 293, 772). Treatment with dilute alcohol gives rhodizonic acid $C_6H_2O_6$ (Heller, Annalen, 1837, 24, 1; 1840, 34, 232; 1862, 124, 32; Will, *ibid.* 1861, 118, 189). Rhodizonic acid, as well as hexahydroxybenzene, when oxidised, give triquinoyl $C_6H_{16}O_{14}$ or $C_6H_6·8H_2O$. Alkalis convert rhodizonic acid into croconic acid $C_5H_2O_5$ (*see* Zincke, Ber. 1887, 20, 1267, footnote), and the latter compound can be oxidised to leuconic acid. All four compounds appear to be cyclic polyketones :



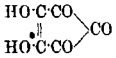
$$\begin{array}{l}HO·C·CO·CO\\ HO\,C·CO·CO\end{array}$$

Rhodizonic acid.



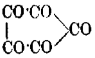
$$\begin{array}{l}CO·CO·CO\\ CO·CO·CO\end{array}$$

Triquinoyl.



$$\begin{array}{l}HO·C·CO\\ HO·C·CO\end{array}\Big\rangle CO$$

Croconic acid.



$$\begin{array}{l}CO·CO\\ CO·CO\end{array}\Big\rangle CO$$

Leuconic acid.

3-*Ethyl*cyclo*pentane*-1 : 2 : 4-trione, m.p. 173° (E. Koenigs and W. Ottmann, Ber. 1921, 54, 1343).

IV. *Aromatic Cyclic Ketones.*

Only the briefest reference can be made to the cyclic ketones, in which both ends of the closed chain containing carbonyl groups are united to aromatic nuclei.

Coumaran $C_6H_4<\substack{CH_2\\O}>CH_2$ gives rise to two ketones, coumaranone $C_6H_4<\substack{CO\\O}>CH_2$, and coumarandione $C_6H_4<\substack{CO\\O}>CO$. The latter compound, despite its name, is really a monoketone, the second carbonyl is lactonic.

Coumaranone $C_6H_4<\substack{CO\\O}>CH_2$ is obtained by the hydrolysis of the esters of coumaranonecarboxylic acid (Friedländer, Ber 1899, 32, 1868); by boiling *ω*-bromo-*o*-acetoxyacetophenone with water and calcium carbonate (F. Ber. 1897, 30, 1081) and by the action of phosphorus pentoxide on phenoxyacetic acid (Störmer and Bartsch, Ber. 1900, 33, 3177). White needles, m.p. 101°–102°. *Oxime*, m.p. 159°; iso*nitroso* derivative, m.p. 172°; this can be regarded as the monoxime of the dione.

Coumaranone is the oxygen analogue of indoxyl and forms a series of 'oxindogenides' (Fries, Ber. 1911, 44, 114, 124). Numerous coumaranone derivatives have been prepared (Merriman, Chem. Soc. Trans. 1911, 99, 911; 1913, 103, 1838, 1845; von Auwers, Annalen, 1912, 393, 338; Ber. 1914, 47, 2334; 1919, 52, 77, 92; 1920, 53, 2271; Higginbotham and Stephen, Trans. Chem. Soc. 1920, 117, 1534)

Coumarandione $C_6H_4<\substack{CO\\O}>CO$ is obtained by dehydration of *o*-hydroxyphenylglyoxylic acid. The carbonyl group in position 2 condenses easily with amino- compounds (Fries and Pfaffendorf, Ber. 1912, 45, 154; Stoermer, *ibid.* 162. *See also* Staudinger, Schlenker and Goldstein, Helv. Chim. Acta, 1921, 4, 334; Stollé and Knebel, Ber. 1921, 54, 1213).

Closely related is 2 : 2′-diketo-Δ1 : 1′-dicoumaran $C_6H_4<\substack{CO\\O}>C\,.\,C<\substack{CO\\O}>C_6H_4$, the so-called 'oxindigo' (Fries, Hasselbach and Schroder, Annalen, 1914, 405, 346).

Benzocoumaranones are described by K. Fries and R. Frellstedt (Ber. 1921, 54, 715).

Hydrindene $C_6H_4<\substack{CH_2\\CH_2}>CH_2$ gives rise to two hydrindones, two diketohydrindenes, and one triketohydrindene. The properties of these compounds are those to be expected of monoketones, α- and *β*-diketones and triketones respectively.

α-Hydrindone $C_6H_4<\substack{CH_2\\CO}>CH_2$. Prepared in several ways. Gently warm ethyl *o*-cyanohydrocinnamate with concentrated hydrochloric acid

$$CN{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2C_2H_5+2H_2O \\ =C_9H_8O+NH_3+CO_2+C_2H_5OH$$

(Gabriel and Hausmann, Ber. 1889, 22, 2018). Distil *o*-carboxyhydrocinnamic acid (König, Annalen, 1893, 275, 342). By the action of aluminium chloride on phenylpropionyl chloride dissolved in petroleum spirit (Kipping, Chem. Soc. Trans. 1894, 65, 485; also Ingold and Thorpe, Trans. Chem. Soc. 1919, 115, 1419), m.p. 40°, b.p. 243°–245°. *Oxime*, m.p. 146°; *semicarbazone*, m.p. 239°.

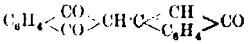
The methylene group adjacent to carbonyl reacts with the aldehyde group and nitrous acid. The *iso*nitroso- compound produced in the latter case is the monoxime of αβ-diketohydrindene. Many derivatives are known.

β-Hydrindone $C_6H_4<\substack{CH_2\\CH_2}>CO$ is obtained by distillation of calcium *o*-phenylenediacetate (Schad, Ber. 1893, 26, 222; Benedikt, Annalen, 1893, 275, 353), and by heating hydrindene glycol with dilute sulphuric acid (Heusler and Schieffer, Ber. 1899, 32, 30), m.p. 58° or 60°, b.p. 220°–225°. *Oxime*, m.p. 155°.

αβ-Diketohydrindene $C_6H_4<\substack{CH_2\\CO}>CO$ results when *iso*-nitroso-*α*-hydrindone is hydrolysed by hydrochloric acid in presence of formaldehyde (Perkin, Roberts and Robinson, Chem. Soc. Trans. 1912, 101, 232). Golden-yellow plates, m.p. 95°–115°. The *oxime*, *semicarbazone*, *quinoxaline*, and *osazone* have been prepared. (*See*, further, Chem. Soc. Trans 1914, 105, 2405; and von Braun, Ber. 1913, 46, 3641; 1916, 49, 1268.)

αγ **Diketohydrindene** $C_6H_4<\substack{CO\\CO}>CH_2$. Phthalic ester and acetic ester are condensed by sodium ethoxide, the resulting diketohydrindene carboxylic ester hydrolysed, and carbon dioxide eliminated from the resulting acid (Gabriel and Neumann, Ber. 1893, 26, 954), m.p. 129°–131°.

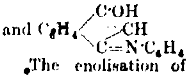
The methylene group is very reactive, and anhydrodiketohydrindene is produced by elimination of water between two molecules (Wislicenus and Kötzle, Annalen, 1889, 252, 76). According to Hantzsch (Annalen, 1912, 392, 322), anhydrodiketohydrindene is



$$C_6H_4<\substack{CO\\CO}>CH{\cdot}C<\substack{CH\\C_6H_4}>CO$$

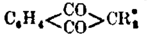
and not $C_6H_4<\substack{CO\\CO}>C:C<\substack{CH_2\\C_6H_5}>CO$

Phenyldiazonium salts give triketohydrindene-*β*-phenylhydrazone

Tautomerism is observed in the derivatives, and whilst the *anil* (m.p. 208°) is probably $C_6H_4<\substack{CO\\ \underset{NC_6H_5}{C}}>CH_2$ in the free state, the salts produced with acids and alkalis are probably derived from the forms $C_6H_4<\substack{CO\\ C\cdot NH{\cdot}C_6H_5}>CH$ and  $C_6H_4<\substack{C{\cdot}OH\\ C{=}N{\cdot}C_6H_5}>CH$ respectively.

The enolisation of 2-monoacylindane-1 : 3-diones may give compounds of the type $C_6H_4<\substack{CO\\CO}>C:CR{\cdot}OH$ (Scheiber and Hopper, Ber. 1920, 53, 697).

Numerous homologues of the type



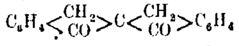
$$C_6H_4<\substack{CO\\CO}>CR_2$$

have been synthesised by Freund and Fleischer (Annalen, 1913, 399, 182; 1913, 402, 51; 1915, 409, 268; 1917, 414, 1; Das and Ghosh, J. Amer. Chem. Soc. 1919, 41, 1221; Fleischer, Annalen, 1921, 422, 231, 265, 272, 317).

Triketohydrindene $C_6H_4<\substack{CO\\CO}>CO$ results on oxidising an alkaline solution of *αγ*-diketohydrindene, with 3–3½ p.c. hydrogen peroxide solution, m.p. 190°–200° (with decomposition)

(Kaufmann, Ber. 1897, 30, 387; *cf.* Ruhemann, Chem. Soc. Trans. 1910, 97, 1438, 2025).

Bis-α-Hydrindene-2 : 2)-spiran

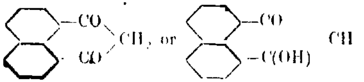


$$C_6H_4<\begin{smallmatrix}CH_2\\CO\end{smallmatrix}>C<\begin{smallmatrix}CH_2\\CO\end{smallmatrix}>C_6H_4$$

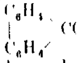
is obtained in small amount by distilling dibenzylmalonyl chloride with 2 p.c. of aluminium chloride under reduced pressure, m.p. 174°, b.p. 255°–257° (Leuchs and Radulesen, Ber. 1912, 45, 189)

1 : 2-**Naphthindandione,** m.p. 180° (Noto, Gazz. chim. ital. 1915, 45, ii. 126).

Perinaphthindandione

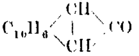


m.p. 265° (Errera, Gazz. chim. ital. 1911, 41, i 190, ii. 807; 1913, 43, ii. 625; Calderaro, *ibid.* 1916, 46, i 261).

Fluorene ketone  $\begin{smallmatrix}C_6H_4\\|\\C_6H_4\end{smallmatrix}>CO$ is obtained by the distillation of calcium diphenate with lime (Fittig and Ostermayer, Annalen, 1873, 166, 373); by oxidation of phenanthraquinone with alkaline permanganate (Anschutz and Japp, Ber. 1878, 11, 212); and by oxidation of fluorene alcohol.

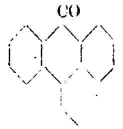
Yellow rhombic tablets, m.p. 83·5°–84°.

A supposed pseudo-form is non-existent (Pummerer, Ber. 1914, 45, 294).

Pyrene ketone  $C_{16}H_8<\begin{smallmatrix}CH\\|\\CH\end{smallmatrix}>CO$ was obtained by Bamberger and Philip by distillation of pyrenic acid $C_{15}H_8O_5$ with slaked lime, m.p. 83°, b.p. 235°–250° (Annalen, 1887, 240, 178).

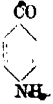
Benzanthrones $C_{17}H_{10}$. These contain benzene and naphthalene residues united directly and also through a carbonyl group.

1 : 9-**Benzanthrone**

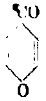


is obtained by heating phenyl-α-naphthyl ketone with 5 parts of aluminium chloride for 5 hours at 150° (Scholl, Annalen, 1912, 394, 111), or by elimination of water from α-naphthylbenzoic acid by means of sulphuric acid (Schaarschmidt, Ber. 1917, 50, 294).

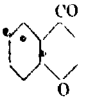
The ketonic properties of the carbonyl group are usually profoundly modified when it forms one of the members of a heterocyclic chain. This is observed in the following well-known examples :—



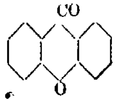
Pyridone.



Pyrone.



Chromone.



Xanthone.

KETONIC ACIDS AND ESTERS.

Whilst a few ketonic acids (*e.g.* pyruvic and lævulic) are obtained by special reactions, these substances are generally obtained as esters by condensation of simpler esters or esters and ketones under the influence of sodium, sodium ethoxide, &c.

α-Ketonic Monobasic Acids.

Pyruvic acid (*Pyroracemic* or *Propanonic acid*) $CH_3{\cdot}CO{\cdot}CO_2H$ can be obtained by the distillation of tartaric or racemic acids (Berzelius, Pogg. Ann. 1835, 36, 1); of glyceric acid (Moldenhauer, Annalen, 1864, 131, 338); and from α-dichloro- or α-dibromopropionic acids or their esters by the action of moist silver oxide (Beckurts and Otto, Ber. 1877, 10, 264; 1885, 18, 228). Claisen and Shadwell hydrolysed acetyl cyanide with hydrochloric acid (Ber. 1878, 11, 620, 1563), and Beilstein and Wiegand oxidised calcium lactate with potassium permanganate (*ibid.* 1884, 17, 840) (*v.* PYRUVIC ACID).

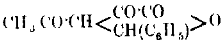
Pyruvic acid is prepared by distilling 500 grams of tartaric acid and 780 grams of commercial potassium bisulphate from a copper retort of 2 litres capacity. The process is complete in 30 minutes, and a 60 p.c. yield is obtained after rectifying the product under reduced pressure, b.p. 59°–60° at 12 mm. (A. Wohl and R. Maag, Ber. 1910, 43, 2188).

The decomposition of tartaric acid on distillation under reduced pressure and at a temperature not much exceeding 180° gives rise to much acetic and less pyruvic acid (Chattaway and Ray, Trans. Chem. Soc. 1920, 119, 34).

The salts crystallise when prepared in the cold; the solutions, if boiled, only yield gummy masses.

The esters hydrolyse very readily (Sudborough, Chem. Soc. Trans. 1912, 101, 1227).

Condensation with benzaldehyde gives ketoacetylphenyl paracone



$$CH_3{\cdot}CO{\cdot}CH<\begin{smallmatrix}CO{\cdot}CO\\CH(C_6H_5)\end{smallmatrix}>O$$

(Mumm, Ber. 1912, 45, 3236). This compound had been previously described by Ruhemann (Chem. Soc. Trans. 1906, 89, 1236).

Pyruvic acid shows the reaction of a (methyl) ketone as well as an acid, *e.g.*

$$CH_3{\cdot}C(OH)(SO_3Na)CO_2H$$

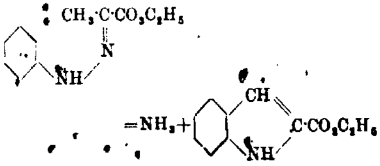
and $CH_3{\cdot}C(OH)(SO_3Na)CO_2Na,H_2O$ are known.

The possibility of the enolisation of derivatives of pyruvic acid is raised by the isolation of an *O*-acetyl derivative of phenylpyruvic acid $C_6H_5{\cdot}CH : C(OCOCH_3){\cdot}CO_2H$ (Bougault and Hemmerlé, Compt. rend. 1915, 160, 100).

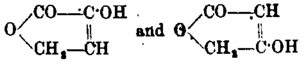
Pyruvic acid phenylhydrazone

$$CH_3{\cdot}C(: N{\cdot}NH{\cdot}C_6H_5)CO_2H$$

forms shining needles, m.p. 192°. The *ethyl ester* $C_9H_9O_2N_2{\cdot}C_2H_5$, m.p. 116°–117°, when heated 3 or 4 minutes with its own weight of zinc chloride, yields ethyl indole carboxylate (E. Fischer, Annalen, 1886, 236, 142):



Tetronic acids, α- and β-. These are lactones of γ-hydroxyketobutyric acids, and are probably to be represented as true enols :



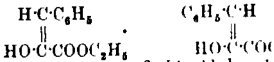
(Wolff and Schwabe, Annalen, 1896, 291, 226; Lapworth, Chem. Soc. Trans. 1915, 107, 135, 1254).

Benzoylformic acid $C_6H_5{\cdot}CO{\cdot}CO_2H$ is obtained by the hydrolysis of benzoyl cyanide with hydrochloric acid (Claisen, Ber. 1877, 10, 845), m.p. 65°–66°; easily soluble in water; reduced by sodium amalgam to mandelic acid, and by hydriodic acid and amorphous phosphorus to α-toluic acid. *Phenylhydrazone*

$$C_6H_5{\cdot}C(:N{\cdot}NH{\cdot}C_6H_5)CO_2H$$

m.p. 153° (with decomposition into carbon-dioxide and benzalphenylhydrazone).

Phenylpyruvic acid $C_6H_5{\cdot}CH_2{\cdot}CO{\cdot}COOH$. Three forms of the ethyl ester are known, to which the following structures are assigned:—



$$\begin{array}{c} H{\cdot}C{\cdot}C_6H_5 \\ \| \\ HO{\cdot}C{\cdot}COOC_2H_5 \end{array} \qquad \begin{array}{c} C_6H_5{\cdot}C{\cdot}H \\ \| \\ HO{\cdot}C{\cdot}COOC_2H_5 \end{array}$$

α. m.p. 51°. β. Liquid, b.p. 149°/15 mm.

$$C_6H_5{\cdot}CH_2{\cdot}CO{\cdot}COOC_2H_5$$

γ. m.p. 79°.

Ethyl β-phenylpyruvate reacts with acid anhydrides and chlorides yielding ethyl acyloxycinnamates, *e.g.*

$$C_6H_5{\cdot}CH:C(OCOCH_3){\cdot}CO_2C_2H_5$$

m.p. 33°–34°. Such derivatives do not form additive compounds with bromine, but immediately discolorise alkaline permanganate (H. Gault and R. Weick, Compt. rend. 1920, 170, 1392; 1920, 171, 305; 1921, 173, 391).

β-Ketonic Monobasic Acids.

The β-ketonic acids are extremely unstable, decomposing very readily into carbon dioxide and a ketone :

$$R{\cdot}CO{\cdot}CH_2{\cdot}COOH = CO_2 + R{\cdot}CO{\cdot}CH_3$$

Owing to the reactivity of the methylene group, the esters of these acids are valuable synthetic agents; they are prepared by the action of sodium (sodium ethoxide, &c.) on esters or mixtures of esters and decomposition of the resultant sodium derivatives with dilute acetic acid :

$$\begin{aligned} R{\cdot}COOC_2H_5 + CH_3{\cdot}COOC_2H_5 + NaOC_2H_5 \\ = 2C_2H_5OH + R{\cdot}C(ONa):CH{\cdot}COOC_2H_5 \\ R{\cdot}C(ONa):CH{\cdot}COOC_2H_5 + H{\cdot}C_2H_3O_2 \\ = Na{\cdot}C_2H_3O_2 + R{\cdot}CO{\cdot}CH_2{\cdot}COOC_2H_5 \end{aligned}$$

Ethyl acetoacetate $CH_3{\cdot}CO{\cdot}CH_2{\cdot}COOC_2H_5$ is obtained by the action of sodium on ethyl acetate (Geuther, J. 1863, 233; Zeitsch. Chem. 1866, 5; Wislicenus, Annalen, 1877, 186, 161; Matthews and Hodgkinson, Ber. 1882, 15, 2679); b.p. 180·6°–181·2°; sp.gr. at 20°/4° 1·0256 (Brühl, Annalen, 1880, 203, 27); b.p. 71° at 12·52 mm. (Kahlbaum). Preparation on large scale (Cobenzl, Chem. Zeit. 1914, 38, 665). Free acetoacetic acid is described by Ceresole as a thickish liquid, miscible with water, reacting strongly acid, and decomposing violently below 100° into carbon dioxide and acetone. Ceresole obtained the acid by allowing 4·5 parts of ethyl acetoacetate, 2·1 parts of caustic potash, and 80 parts of water to stand for 24 hours, then acidifying with sulphuric acid and extracting with ether (Ber. 1882, 15, 1327, 1872).

In addition to the use of acetoacetic ester in the laboratory, it is employed in the preparation of pyrazolone derivatives, *e.g.* antipyrine and pyrazolone dyestuffs (*see* Farbenfab. vorm. Fr. Bayer & Co., Eng. Pat. 532 of 1910 (*v.* PYRAZOLONE).

Ethyl acetoacetate reacts tautomerically as $CH_3{\cdot}C(OH):CH{\cdot}CO_2C_2H_5$ and $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO_2C_2H_5$

Knorr, Rothe, and Averbeck (Ber. 1911, 44, 1138) have isolated the two forms, the ketonic ester being sparingly soluble in organic solvents at low temperatures. Both forms may be distilled in a high vacuum with little change. Ketonic ester, b.p. 40°–41°/2 mm., n_D^{10} 1·4225; enolic ester, b.p. 33°, n_D^{10} 1·4480. For the equilibrium mixture, b.p. 39°–40°/2 mm., n_D^{10} 1·4230 to 1·4232.

K. H. Meyer and V. Schoeller find that when ethyl acetoacetate is distilled from a glass vessel at 2 mm. pressure, the distillate is far richer in the enolic form (about 70 p.c.), whilst the residue contains only 5 p.c. of enol. The enolisation is due to the catalytic action of the glass, for on distilling from a silica flask, three fractions and a residue, all of equal volume, gave 22, 11, 2·5 and 0 p.c. respectively. Hence the best way of obtaining the pure ketonic form is to distil under "aseptic" conditions (Ber. 1920, 53, 1410).

The pure enol may be obtained by distilling the equilibrium ester from a Jena glass vessel in presence of a trace of phthalic acid. The distillate, containing 88 p.c. enol, is collected in a quartz vessel and immediately refractionated from a silica apparatus, the pure enol forming the first fraction; n_D^{10} 1·4475. The method has also been applied to the preparation of enolic acetylacetone, which was obtained with about 1 p.c. of the ketone; n_D^{10} 1·4025 (K. H. Meyer and H. Hopff, Ber. 1921, 54, 579).

The question of this tautomerism has been much discussed, some of the papers bearing on this matter which have appeared since 1890 are as follows :—

J. U. Nef (Annalen, 1891, 266, 52; 1893, 276, 239); W. H. Perkin, sen. (Chem. Soc. Trans. 1892, 61, 800); J. W. Brühl (Ber. 1894, 27, 2378; J. pr. Chem. 1894, [ii.] 50, 119); L. Claisen (Annalen, 1893, 277, 162; Ber. 1892, 25, 1763); A. Michael (Amer. Chem. J. 1892, 14, 481; Ber. 1905, 38, 22; *cf.* H. Goldschmidt, *ibid.* 1096); A. Lapworth (Chem. Soc. Trans. 1902, 81, 1491, 1499; 1903, 83, 1114; 1904, 85, 30, 46; 1908, 93, 30; 1911, 99, 1882); E. C. C. Baly and C. H. Desch (*ibid.* 1904, 85, 1029; 1905, 87, 766); R. S. Morrell (Chem. Soc. Proc. 1898, 14, 121; Chem. Soc. Trans. 1903, 83, 1292); R. Schenck and E. Ellenberger (Ber. 1904, 37, 3446); F. Giolitti (Gazz. chim. ital. 1904, 34, ii. 208); S. F. Acree (Amer. Chem. J. 1907, 37, 71); A. E. Dunstan and J. A. Stubbs (Chem. Soc. Trans. 1908, 93, 1919); A. Hantzsch (Ber. 1910, 43, 3049; *ibid.* 1911, 44, 1771);

Dawson and co-workers (Chem. Soc. Trans. 1909, 95, 1860; 1910, 97, 2048; 1911, 99, 1, 1740; 1912, 101, 1503); Knorr (*ibid.* 1911, 44, 1138, 2767); Kurt Meyer (Annalen, 1911, 380, 212; Ber. 1911, 44, 2718, 2725, 2729; 1912, 45, 2843; Annalen, 1913, 398, 49).

A coloration with ferric chloride is produced by enolic modifications of ketones and ketonic esters, and not by the ketonic forms.

In arriving at a decision as to the proportion of ketone and enol in an equilibrium mixture, either physical or chemical methods may be employed. The β-ketonic esters and 1 : 3-diketones have been specially examined, and, of the physical methods, those depending on optical properties have received most attention. Thus, W. H. Perkin, sen., made use of magnetic rotation, Bruhl of refraction and dispersion, whilst Hantzsch (Ber. 1915, 48, 1407) photographed absorption spectra. The results obtained by different methods have not always agreed, much depending on the interpretation of the measurements. A further complication is caused by the displacement of equilibrium when a solvent is employed, as in the case of photographing absorption spectra.

Of purely chemical methods of determining the proportion of enol in a mixture, that due to Kurt Meyer is important. The substance is dissolved in alcohol, alcoholic solution of bromine added until the colour is no longer discharged and the excess of bromine removed by alcoholic β-naphthol. The bromo-ketone derived from the enol is then reduced by excess of potassium iodide

$$\cdot CO\cdot CBr< + 2KI + H_2O \quad CO\cdot CH< + KOH + I_2$$

and the liberated iodine estimated with $N/10$-thiosulphate

Ordinary ethyl acetoacetate consists of about 92·6 p.c. of the keto and 7·4 p.c. of the enol modification. Water favours the keto-form, whilst dilution with hexane enolises the ester.

The proportion of enol present in equilibrium mixtures as determined by refractometric and chemical methods do not always agree. When a simple ketone is in question, a decision between ·CO·CHR· and C(OH) : CR· is easy to arrive at.

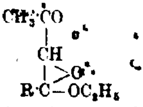
In the case of diketones, von Auwers (Annalen, 1918, 415, 169) shows that useful results may be obtained from refractometric measurements, if due allowance be made for the exaltation caused by conjugation when the grouping ·C(OH) : CR·CR : O occurs.

This can be done if compounds containing the groupings

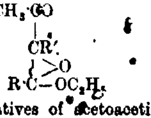
$$\cdot CH:CH\cdot CR:O \quad \text{and} \quad \cdot CH:CH\cdot C(OH):O$$

as well as substitution derivatives are measured, and the results compared with those obtained from the substance under examination.

Deductions have also been drawn from a study of the products obtained on electrolytically reducing aceto-acetic ester and its derivatives. Tafel has considered constitutions such as



and



for the substitution derivatives of acetoacetic ester (Ber. 1907, 40, 3312; 1909, 42, 2548; 1912, 45, 437). A useful account of tautomerism, including that of the ketones and ketonic esters, is given in the Presidential Address by W. H. Perkin, jun. (Chem. Soc. Trans. 1914, 105, 1176).

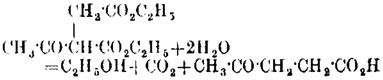
The electronic constitution of acetoacetic acid is discussed by Hauke and Noessler (J. Amer. Chem. Soc. 1918, 40, 1726).

Oxidation of sodium acetoacetate with potassium permanganate gives acetic, oxalic and glyoxylic acids (Engfeldt, Zeitsch. physiol. Chem. 1921, 112, 176).

Ethyl γ-chloroacetoacetate (J. F. Hamel, Bull. Soc. chim. 1921, [iv.] 29, 390) is converted by sodium ethoxide or phenoxide into ethyl succinylsuccinate, m.p. 126–127° (Sommelet, *ibid.* 102, 553).

γ-Ketonic Monobasic Acids.

Lævulic acid $CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CO_2H$ is obtained synthetically from diethyl acetosuccinate (b.p. 254°–256°, sp.gr. 1·08809 at 15°), produced from ethyl chloroacetate and the sodium derivative of ethyl acetoacetate by boiling with twice its volume of dilute hydrochloric acid (Conrad, Annalen, 1877, 188, 222):



$$\begin{array}{l} \quad\quad CH_2\cdot CO_2C_2H_5 \\ \quad\quad | \\ CH_3\cdot CO\cdot CH\cdot CO_2C_2H_5 + 2H_2O \\ \quad = C_2H_5OH + CO_2 + CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CO_2H \end{array}$$

It is obtained from various carbohydrates by boiling with acids *e.g.* lævulose, glucose, cane sugar, milk sugar, inulin (Tollens, Annalen, 1875, 175, 181; 1881, 206, 231; 1885, 227, 228); pine shavings, Carragheen moss and gum arabic (Bente, Ber. 1875, 8, 416, 1157). Conrad and Guthzeit (*ibid.* 1885, 18, 1442) recommend warming 20 grams of cane sugar with 50 grams of water containing 9·43 grams of hydrogen chloride for 17 hours on the water-bath. The liquid is filtered, evaporated on the water-bath, and extracted with ether; the ethereal extract is concentrated and distilled under reduced pressure.

W. A. van Ekenstein and J. J. Blanksma find the conversion of hexoses into lævulic acid takes place in two stages, hydroxyfurfuraldehyde which is first formed, giving lævulic and formic acids subsequently (Chem. Weekblad, 1910, 7, 387).

Lævulic acid has m.p. 33·5°, b.p. 250° (with slight decomposition); sp.gr. 1·135 at 15°. Optical constants (von Auwers and Heinze, Ber. 1919, 52, 584). Easily soluble in water, alcohol, and ether. Reduced by sodium amalgam in alcoholic solution to γ-hydroxyvaleric acid. Yields iodoform with iodine and caustic soda in the cold and forms *oxime* and *phenylhydrazone*, m.p. 108°. The latter compound loses water above 160°, giving phenylmethylpyridazolone $CH_3 \lessgtr \begin{array}{l} CH_2-CH_2 \\ N\cdot N(C_6H_5) \end{array} > CO$.
The *methyl* and *ethyl esters* are liquid, and boil at 191°–191·5° (743 mm.) and 205·2° (corr. 756 mm.) respectively.

Lævulic acid is used in cotton printing.

γ-Ketonic acids condense in some cases with aldehydes; *e.g.* sodium benzoyl propionate, acetic anhydride and benzaldehyde give phenylbenzylidenecrotonolactone (W. Borsche, Ber. 1914, 47, 1108).

The synthesis of esters of δ-ketonic acids due to Kohler, has been extended by Hahn and Allbee (Amer. Chem. J. 1913, 49, 171).

A number of ε-ketonic acids have been prepared, starting with adipic acid (E. E. Blaise and A. Koehler, Bull. Soc. chim. 1910, [iv.] 7, 215).

Carboxylic acids of cyclic ketones are also known, *e.g. cyclo*hexanone-2-carboxylic acid, and 1-methyl*cyclo*hexane-2-one-3-carboxylic acid (H. D. Gardner, W. H. Perkin, jun., and H. Watson, Chem. Soc. Trans. 1910, 97, 1756).

Dibasic Ketonic Acids.

Mesoxalic acid (dihydroxymalonic acid) $C(OH)_2(COOH)_2$ or $CO(COOH)_2.H_2O$ was obtained by Liebig and Wöhler by the hydrolysis of alloxan (Annalen, 1838, 26, 298); from aminomalonic acid by Baeyer (*ibid.* 1864, 131, 298) and from dibromomalonic acid by Petriew (J. Russ. Phys. Chem. Soc. 1878, 10, 72). M. Conrad and C. Brückner (Ber. 1891, 24, 2993) obtained the diethyl ester (m.p. 57°) by the action of bromine on diethyl acetyltartronate $CH_3CO\cdot O\cdot CH(CO_2C_2H_5)_2$, whilst H. Filippo, jun., obtained a practically quantitative yield of the ester by the action of bromine on diethyl tartronate (Rec. trav. chim. 1910, [ii.] 14, 113).

Mesoxalic acid melts at 119°–120° (E. Fischer), is easily soluble in water, fairly so in alcohol and ether. The aqueous solution, when boiled, gradually decomposes into carbon dioxide and glyoxylic acid.

The mesoxalic and oxomalonic esters are obtained by acting on the corresponding malonic esters in admixture with acetic anhydride and ether with the nitrous gases evolved by the action of water on nitroxyl sulphate (Schmitt, Compt. rend. 1905, 140, 1400; Curtiss, Amer. Chem. J. 1906, 35, 477; J. Amer. Chem. Soc. 1908, 30, 1264; Meyer, Bull. soc. chim. 1911, iv. 9, 423).

Another example of the conversion of a malonic into a mesoxalic derivative is afforded by the formation of dithiomesoxanilide from malonanilide and sulphur monochloride (Naik, Trans. Chem. Soc. 1921, 119, 382, 1231).

Diethyl oxalacetate

$$C_2H_5O_2C\cdot CO\cdot CH_2\cdot CO_2C_2H_5$$

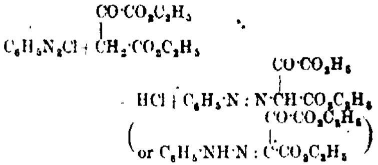
is obtained by Claisen's method from diethyl oxalate and ethyl acetate, and by the action of concentrated sulphuric acid on diethyl acetonedicarboxylate. It is a colourless oil giving an intense dark red coloration with ferric chloride, and is sufficiently acid in character to be titrated with phenolphthalein as indicator (H. Gault, Compt. rend. 1910, 150, 1608; L. J. Simon, *ibid.* 1760).

Hydrolysis with dilute sulphuric acid gives alcohol, carbon dioxide, and pyruvic acid (ketonic fission); with alkalis, salts of oxalic and acetic acids are produced.

The sensitiveness of esters of oxalacetic ester to alkalis is considerable, traces being sufficient to bring about marked decomposition. The dimethyl ester gives m.p. 87°–90° in Jena glass, but only 7[illegible]° if heated in a soft glass tube (Dieckmann, Ber. 1916, 49, 2213).

On lactonisation, oxalacetic ester gives oxalocitrolactone (Gault, Compt. rend. 1914, 158, 711).

The ester reacts with phenyldiazonium chloride, giving a product identical with the monophenylhydrazone of diethyl diketosuccinate (m.p. 72°–73°):

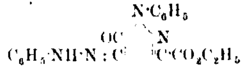


$$\begin{array}{l} \phantom{C_6H_5N_2Cl+{}}CO\cdot CO_2C_2H_5 \\ C_6H_5N_2Cl+CH_2\cdot CO_2C_2H_5 \end{array}$$

$$= HCl + C_6H_5\cdot N:N\cdot\overset{CO\cdot CO_2H_5}{CH}\cdot CO_2C_2H_5$$

$$\left(\text{or } C_6H_5\cdot NH\cdot N:\overset{CO\cdot CO_2C_2H_5}{C}\cdot CO_2C_2H_5\right)$$

The action of phenylhydrazine on this compound yields an osazone (m.p. 119°–120°) $\begin{array}{l}C_6H_5\cdot NH\cdot N:C\cdot CO_2C_2H_5\\ C_6H_5\cdot NH\cdot N:C\cdot CO_2C_2H_5\end{array}$, identical with the product obtained by Anschutz and Geldermann from phenylhydrazine and diethyl diketosuccinate (Annalen, 1891, 261, 130). When this osazone is boiled with three or four parts of glacial acetic acid, ethyl alcohol is eliminated, and ethyl phenylketopyrazolonephenylhydrazone carboxylate



is produced (W. Wislicenus and A. Jensen, Ber. 1892, 25, 3448). Orange needles, m.p. 152°–153°; also obtained by Anschutz and Parlato (*ibid.* 1892, 25, 1975).

The pyrazolone compound described is of tartrazine type, and it is evident that mixed tartrazines may be prepared from ethyl oxalacetate, using hydrazines and diazo compounds derived from different aromatic amines. The constitution of the original tartrazine derived from phenylhydrazine-*p*-sulphonic and dihydroxytartaric acids has been fully investigated by Anschutz (Annalen, 1897, 294, 219), who recognised definitely the existence of the pyrazolone ring in the dyestuff. In the preparation of this colouring matter from diethyl oxalacetate, 9·4 kilos. of the ester, 9·5 kilos. of phenylhydrazine sulphonic acid, and 7·5 kilos. of crystallised sodium acetate are stirred with 50 litres of water at 50° until complete solution is effected. The solution is cooled to ordinary temperature, 8–10 kilos. of calcined soda are added (reaction alkaline), and after completion of the pyrazolone condensation, the tartrazinogen ester sulphonic acid precipitated by dilute sulphuric acid, pressed and dried. After the hydrolysis with caustic soda, diazotised sulphanilic acid is added, and the tartrazine salted out when coupling is completed (B. A. S. F., Eng. Pats. 5693 of 1893 and 705 of 1897; *cp.* R. Gnehm and L. Benda, Annalen, 1898, 299, 100, and Farbenfab. vorm. Fr. Bayer & Co., Eng. Pat. 532 of 1910).

Dihydroxytartaric acid (Diketosuccinic acid)

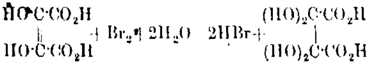
$$HO_2C\cdot C(OH)_2C(OH)_2\cdot CO_2H \text{ or } HO_2C\cdot CO\cdot CO\cdot CO_2H+2H_2O$$

was first obtained from protocatechuic acid (Gruber, Ber. 1879, 12, 514) and catechol (Barth, Monatsh. 1880, 1, 869) by the action of nitrous gases (N_2O_3). Kekulé obtained it from dinitrotartaric acid

$$HO_2C\cdot CH(O\cdot NO_2)\cdot CH(O\cdot NO_2)\cdot CO_2H$$

(Annalen, 1883, 221, 247). The dinitrotartaric acid is obtained by dissolving tartaric acid in 4½ parts of fuming nitric acid, shaking with an equal volume of concentrated sulphuric acid, and drying the precipitate on porous earthen ware. This compound is then mixed with an equal amount of ether, some crude ethyl nitrite added, and the mixture allowed to stand for some days. On shaking with water and adding sodium carbonate, the nearly insoluble sodium dihydroxytartrate is precipitated.

H. J. H. Fenton and E. S. St. B. Sladen (Eng. Pat. 27032 of 1897) obtain the acid by adding to a mixture of 1 part of dihydroxymaleic acid and 4 parts of glacial acetic acid, bromine and water drop by drop in quantities slightly greater than that required by the equation



$$\begin{array}{l}HO\cdot C\cdot CO_2H\\ \quad \| \\ HO\cdot C\cdot CO_2H\end{array} + Br_2 + 2H_2O \quad 2HBr + \begin{array}{l}(HO)_2C\cdot CO_2H\\ \quad | \\ (HO)_2C\cdot CO_2H\end{array}$$

During the addition the mixture is well cooled.

Dihydroxytartaric acid generally reacts as diketosuccinic acid, and is very unstable; its employment in the production of tartrazines has already been mentioned.

Acetonedicarboxylic acid

$$HO_2C\cdot CH_2\cdot CO\cdot CH_2\cdot CO_2H$$

is obtained by heating citric and sulphuric acids on the water-bath until carbon dioxide begins to be evolved:

$$HO_2C\cdot CH_2\cdot C(OH)(CO_2H)CH_2\cdot CO_2H$$
$$= HO_2C\cdot CH_2\cdot CO\cdot CH_2\cdot CO_2H + H\cdot COOH(CO + H_2O)$$

The mixture is then diluted with water, and the acetonedicarboxylic acid extracted with ether (v. Pechmann, Ber. 1884, 17, 2543). By using hydrated citric acid and forming sulphuric acid (20 p.c. SO_3), Willstatter and Pfannenstiehl have obtained yields of 58 to 86 p.c. (Annalen, 1921, 422, 1).

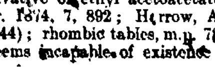
Acetonedicarboxylic acid is obtained crystalline from ethyl acetate; it decomposes on fusion into carbon dioxide and acetone, the same reaction occurring on boiling with water or warming with acids or alkalis. Ferric chloride gives a violet coloration. M.p. 138°.

Heated with phenylhydrazine and hydrochloric acid in aqueous solution, methylphenylpyrazolone carboxylic acid is produced. The latter compound, when heated to 160°, and then distilled under reduced pressure, gives Knorr's phenylmethylpyrazolone (Ber. 1883, 16, 2597; Annalen, 1887, 238, 147; v. Pechmann and Jenisch, Ber. 1891, 24, 3252).

Condensations with aldehydes, ammonia and amines (Petrenko-Kritschenko, J. pr. Chem. 1912, ii. 85, 1).

Electrolysis of ethyl potassio-acetone dicarboxylate after neutralisation with 1·2N-oxalic acid at 0° gives ethyl ββ′-diketo suberate (succinyldiacetate), m.p. 46°–47°. The corresponding free acid melts at 117°.

Diethyl diacetosuccinate



$$\begin{array}{l}CH_3\cdot CO\cdot CH\cdot CO_2C_2H_5\\ \qquad\qquad\ |\\ CH_3\cdot CO\cdot CH\cdot CO_2C_2H_5\end{array}$$

is obtained by the action of iodine on the sodium derivative of ethyl acetoacetate (Rugheimer, Ber. 1874, 7, 892; Harrow, Annalen, 1880, 201, 144); rhombic tables, m.p. 78°. The free acid seems incapable of existence; when boiled with 20 p.c. sodium carbonate solution carbon dioxide escapes and acetonylacetone is produced. Like the latter compound, the ester readily condenses with ammonia, giving pyrrol derivatives.

Ethyl oxalyl-succinate, b.p. 170°–175°/12–13 mm. (Blaise a. Gault, Bull. Soc. Chim. 1911, 9, 451, 458, 588; *see* also Wislicenus and Waldmüller, Ber. 1911, 44, 1564).

Ethyl diketobutyrate is obtained by the action of nitrous gases on ethyl *iso*nitrosoacetoacetate. B.p. 70°/13 mm. Forms a crystalline hydrate $C_6H_8O_4,\frac{1}{2}H_2O$, m.p. 120° (Bouveault and Wahl, Compt. rend. 1904, 138, 1221; Wahl, *ibid.* 1907, 144, 212; 1911, 152, 95; 1912, 154, 1237). The *dimethylamino-anil*, m.p. 63·5°, is obtained by the action of nitrosodimethylaniline on ethyl acetoacetate (Sachs, Ber. 1903, 36, 3221). Formation of lactones (Gault, Compt. rend. 1911, 153, 107).

ALDEHYDE-KETONES.

Compounds are known containing carbonyl in both aldehyde and ketone groups; the two simplest compounds of this class are methylglyoxal and mesoxal dialdehyde.

Methylglyoxal $CH_3\cdot CO\cdot CHO$ was first obtained as a dipolymeride together with acetone peroxide by gently warming mesityl oxide ozonide (Harries and Türk, Ber. 1905, 38, 1630). The acetal $CH_3\cdot CO\cdot CH(OC_2H_5)_2$ is obtained from ethyl diethoxyacetate and methyl magnesium iodide (Wohl and Lange, Ber. 1908, 41, 3612), and when hydrolysed by dilute sulphuric acid gives the tripolymeride of methylglyoxal. The monomolecular form is obtained by distilling the tripolymeride under reduced pressure; it is an intensely yellow liquid with a pungent odour. It begins to boil at 72°, but polymerises (Meisenheimer, Ber. 1912, 45, 2635).

Methylglyoxal is an intermediary product of sugar degradation by weak alkalis (sodium carbonate or phosphate), in presence of phenylhydrazine the osazone is obtained, a particularly good yield being obtained when fructose is the sugar employed (Neuberg and Oektel, Biochem. Zeitsch. 1913, 55, 495).

For preparation of glyoxals of the type $R\cdot CO\cdot CHO$ and their acetals, *see* Dakin and Dudley (Chem. Soc. Trans. 1914, 105, 2453).

Mesoxaldialdehyde $CHO\cdot CO\cdot CHO$ is obtained as a hydrate by the decomposition of phorone diozonide with ice water. The anhydrous compound forms a pale yellow, brittle, hygroscopic mass (Harries and Türk, Ber. 1905, 38, 1630). A solution may also be obtained by passing nitrous fumes into an ice-cold aqueous suspension of diisonitrosoacetone (Henle and Schupp, Ber. 1905, 78, 1372).

The *triphenylhydrazone* prepared from mesoxaldialdehyde melted at 156° (Harries and Türk), though when obtained from acetonedicarboxylic acid and phenyldiazonium chloride the m.p. was found to be 175°–176° (von Pechmann and Jenisch, Ber. 1891, 24, 3255).

J. T. H.

KETOXIMES. Substances formed by the action of hydroxylamine on ketones.

KHARSIVAN. Syn. for Salvarsan.

KHAYA or **KAYA** *v.* CAIL-CEDRA.

KIDNEY-IRON-ORE *v.* HÆMATITE and IRON.

KIESELGUHR *v.* Diatomite.

KIESERITE. Hydrated magnesium sulphate $MgSO_4,H_2O$, of rare occurrence as colourless monoclinic crystals; but as finely granular to compact masses of a greyish-white colour it is abundant in the potash-salt deposits of Stassfurt in Prussia. It is also found at Hallstadt in Austria, and Kalusz in Poland. Sp.gr. 2·57; H. 3–3½. On exposure to air it gradually becomes opaque and falls to a white powder, due to the absorption of water and conversion into epsomite. The 'kieserite zone,' about 60 metres in thickness and consisting of kieserite, together with carnallite, bischofite, rock-salt, and anhydrite, lies immediately below the 'carnallite zone' (*v.* Potassium). (On the artificial production of kieserite, *see* van 't Hoff, Sitz.-Ber. Akad. Wiss. Berlin, 1901, 1034.)

L. J. S.

KILLAS. A local name used by Cornish miners for the clay-slates of their country (*v.* Slate).

KINETATE *v.* Explosives.

KINETINE. A combination of quinine and hedine.

KINEURINE. Trade name for quinine glycerophosphate.

KING'S BLUE, KING'S YELLOW *v.* Pigments.

KINO of the B. P. and U.S. P. is the juice, dried by heat, which is obtained from incisions in the trunk of *Pterocarpus Marsupium* (Roxb.) (Corom. Pl. plate 116; Bentl. a. Trim. plate 81), a tall tree of Southern India and Ceylon, the felling of which is restricted by the Government in the Madras Presidency. This *East Indian, Malabar, Madras,* or *Cochin* kino forms small, angular, glistening, opaque, reddish black, brittle fragments, transparent and ruby-red in thin laminæ. It has a very astringent taste, colours the saliva blood-red, and dissolves almost entirely in 90 p.c. alcohol, slowly and incompletely in cold water; in hot water at least 75 p.c. dissolves. The ash does not exceed 2·5 p.c. (B. P.). Fused with potash it gives about 9 p.c. of phloroglucinol (Hlasiwetz, Annalen, 134, 122) and protocatechuic acid. Dry distillation yields catechol, and ether also extracts a little of this substance. Dilute mineral acids precipitate from the aqueous solution *kinotannic acid*, the principal constituent (75–80 p.c.), which is coloured green by ferric chloride and has not been obtained pure. By boiling kino with dilute hydrochloric acid (1 in 5) a colourless crystalline compound *kinoïn* $C_{14}H_{12}O_6$ is extracted, which can be removed from the acid solution by ether and crystallised from water; about 1·5 p.c. is present (Etti, Ber. 1878, 11, 1879; 1884, 17, 2241). Kinoïn gives with ferric chloride a red colour and is decomposed by concentrated hydrochloric acid at 120°–130° into methylchloride, gallic acid, and catechol, which indicates that it is perhaps guical gallate $C_6H_2(OH)_3CO\cdot OC_6H_4OMe$. Heated by itself at 120°–130° it forms the anhydride *kino red* $C_{28}H_{22}O_{11}$, which is also obtained from the residues after extracting kinoïn from kino by means of acid.

Another variety of Indian kino is obtained from *Butea frondosa* (Roxb.), and is known as *Butea gum, Butea gum, Bengal kino, Palas* or *Pulas kino,* or *Dhak gum.* Only about 40 p.c. is soluble in 90 p.c. alcohol, but in other respects it closely resembles kino from *Pterocarpus Marsupium*, for which the B. P. allows it to be substituted in India and the East, under the name *Buteæ Gummi.*

Australian, Botany Bay or *Eucalyptus kino, Eucalyptus gum* or *red gum* is derived from various species of *Eucalyptus* (Mueller, Pharm. J. [iii.] 16, 898; Maiden, J. Soc. Chem. Ind. 1888, 38; Pharm. J. [iii.] 20, 221, 321), and is also included in the B. P. (*Kino eucalypti*). G. B.

KINO RED, KINOÏN, KINOTANNIC ACID, *v.* Kino.

KIRSCHWASSER or **KIRSCH** is a strong spirituous liquor made by distillation of the fermented juice of ripe Morella or wild cherries. It is prepared chiefly in Germany (particularly in the Black Forest), in Switzerland, and in the Vosges district in France.

The cherries are crushed and the juice collected in vats, the kernels added and the whole allowed to ferment for about 5 days, when the liquor is drawn off and distilled by steam.

The strength of the spirit is usually about 50 p.c. alcohol by volume or approximately 10 under proof; and its peculiar taste and flavour are due largely to the presence of hydrocyanic (prussic) acid derived from the kernels of the cherry stones.

In properly made kirschwasser, the hydrocyanic acid does not exceed 0·015 gram per litre, but in crude varieties, made by prolonged fermentation of unripe or unsound fruit, and distilled over an open fire, it occasionally reaches almost poisonous proportions.

Kirschwasser is sometimes made from grain, grape, molasses, or other spirit flavoured with 'essence of kirschwasser' or with peach blossom, oil of bitter almonds or its substitute, nitrobenzene. Traces of copper are frequently found as an impurity, due no doubt to the copper vessels used for distillation.

Genuine kirschwasser improves greatly by keeping, either in flasks or bottles with porous stoppers or in casks. The latter are made of ash in preference to oak, as the liquor should remain perfectly bright and colourless.

Various imitations of kirschwasser are made, the characteristic flavour being derived from the kernels of stone fruit, apricots, peach kernels or oil of bitter almonds. The following recipe (Spon's Encyclopædia) is one of the best: cherry seeds, 9 kilos.; apricot seeds, 3 kilos.; dried peach leaves, 625 grams; myrrh, 150 grams; alcohol at 85°, 62 litres. The seeds are bruised and digested with about 30 litres of water for 24 hours, and the whole distilled until about 60 litres have come over, when the distillate is reduced to about 50° alcohol. A little glycerin or sugar (not more than 15 grams per 100 litres) is usually added to soften the flavour.

Kirschwasser is occasionally heavily sweetened, when it greatly resembles 'noyeau' (*v.* Liqueurs and Cordials). J. C.

KISH. An ironworker's name for the masses of impure graphite which are occasionally found in blast furnaces, and which separate out from molten cast iron.

KLIACHITE *v.* Bauxite.

KOHLRABI. *Brassica oleracea* f. *caulo-rapa.* A plant of the cabbage tribe producing a great enlargement on the stem. This 'bulb,' which sometimes weighs as much as 12 or 15 lbs., is the valued portion of the crop, and furnishes an excellent substitute for swedes or turnips as food for cattle and sheep.

It is very hardy and more resistant to drought and frost than the turnip.

König gives as the average composition of the 'bulb'—

Water	Protein	Fat	Sugar	Other N-free subst.	Crude fibre	Ash	Organic sulphur
86·9	2·9	0·2	0·4	7·8	1·7	1·2	0·06

Of the total nitrogen, from which the 'protein' in the above analysis is calculated, only about 44 p.c. is present as true proteid, about 8 p.c. as amides, and the remainder in other forms of combination.

The leaves and stalks contain—

Water	Protein	Fat	Sugar	Other N-free subst	Crude fibre	Ash	Organic sulphur
80·0	3·9	0·4	0·5	6·8	1·6	1·7	0·08

The ash contains—

	K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	SiO_2	Cl	
'Bulb'	35·3	6·5	11·0	6·8	3·0	21·0	8·8	2·5	4·9	p.c.
Leaves	18 5	4·9	30·1	4·6	6·0	8·3	10·9	9·0	8·0	,,

H. I.

KOLA. Kola nuts, the fruit of *Cola acuminata* (Schott and Endl.), are imported from the West Coast of Africa, and are made into a paste which contains about 2 p.c. of caffeine, in addition to betaïne (Polstorff, Chem. Zentr. 1909, ii. 1014; *cf.* Desvignes, J. Pharm. Chim. 1910, 2, 20; Allard, *ibid.* 2, 122). According to Heckel and Schlagdenhauffen, the fruit of *Heritiera littoralis* (Dryand), a tree growing in India, in the Philippines, and Molucca, is often found mixed with kola nuts. This fruit belongs to the same family (*Sterculiaceæ*) as those which give the kola nuts, and is said to possess the same waste-repairing properties as the kola nut, although it contains no caffeine. It is used as a foodstuff in India.

KONDANG WAX *v. Figtree Wax,* art. Waxes.

KORALLENERZ *v.* Cinnabar.

KORONIUM BROMIDE. A trade name for strontium bromide.

KOSIN or **KOUSSEIN RESIN** *v.* Resins.

KOUMISS *v.* Milk.

KOUSSO or **CUSSO,** B.P. The dried panicles of pistillate flowers of *Brayera anthelmintica* (Kunth.) *v.* Resins.

KRAMERIA ROOT *v.* Rehatany root.

KRANTZITE. A variety of retinite (*v.* Resins).

KREMS or **KREMSER WHITE, CREMNITZ WHITE,** *v.* Pigments.

KREOLIN. Trade name for a preparation of crude carbolic acid. Used as an antiseptic.

KREOSAL, KREOTOSAL, KRESALOL, KYROGENIN, *v.* Synthetic drugs.

KREOSOL *v. Guaiacum,* art. Resins.

KRESAMINE. Ethylene diamine tricresol.

KRESAPOLIN, KRESOLIN. Preparations of crude carbolic acid. Used as disinfectants.

KRESATIN. *m*-Cresol acetate.

KRYOFINE. Trade name for phenetidine-methyl-glycollate $CH_3OCH_2CONH{\cdot}C_6H_4OC_2H_5$. Used as an antipyretic and anti-neuralgic. White crystalline needles, m.p. 98°, odourless and tasteless, sparingly soluble in water (*v.* Synthetic drugs).

KRYPTON. Sym. Kr. At.wt. 82·9 (Moore, Watson, *v. infra*).

An inert gas, discovered by Ramsay and Travers (Proc. Roy. Soc. 1898, 63, 405; British Assoc. Rep. 1898, 828) in the last portions of gas collected after evaporating considerable quantities of liquid air. When the latter is allowed to evaporate quietly in a vacuum vessel, the last traces of liquid consist almost entirely of oxygen, with small quantities of nitrogen, argon, krypton, and xenon. The liquid is allowed to evaporate, the gas is mixed with hydrogen and passed through a heated iron tube to remove oxygen. Nitrogen is absorbed by means of lime and magnesium (*cf.* Argon), and after removing traces of hydrogen and carbon monoxide by means of heated copper oxide, the mixture of argon, krypton, and xenon is separated into its components by liquefaction and fractional evaporation. At the temperature of liquid air, krypton has a vapour pressure of 17 mm., whilst that of xenon is only 0·17 mm. (*v.* Travers, Study of Gases, 218; Ladenburg and Krügel, Sitzungber. K. Preuss. Akad. Wiss. 1900, 212, 727; Ramsay and Travers, Proc. Roy. Soc. 1901, 67, 329; Moore, Chem. Soc. Trans. 1908, 93, 2181). The separation of a mixture of argon, krypton, and xenon has been effected by absorbing the gases in charcoal cooled in liquid air, allowing the temperature to rise slowly and collecting the evolved gas in fractions (Valentiner and Schmidt, Sitzungber. K. Akad. Wiss. Berlin, 1905, 38. 816).

The proportion of krypton in the atmosphere is about 1 part in twenty millions by volume (Ramsay, Proc. Roy. Soc. 1903 71, 421; 1908, 80, A. 599); $50+10^{-9}$ by volume, $140+10^{-9}$ by weight (Leduc Bureau, Int. Poids et Mes. Mem. 16, 1917). Krypton also occurs in the gases evolved from many thermal springs (Moureu and Lepape, Compt. rend. 1909, 149, 1171).

Krypton is a colourless, odourless, tasteless gas. It is only slightly soluble in water, the absorption coefficient at 0°, 0·1095; 10°, 0·0807; 20°, 0·0626; 30°, 0·0511 (Antropoff, Zeitsch. Elektrochem. 1919, 25, 269). One litre of the gas at N. T. P. weighs 3·708 grams; its density is therefore 41·506 (O=16) (Moore, Chem. Soc. Trans. 1908, 93, 2181; Watson, *ibid.* 1910, 97, 833). Krypton boils at −151·7° and melts at −169°; its critical temperature is −62·5°, and the critical pressure is 54·3 atmospheres. One cub. cm. of liquid krypton at its boiling-point weighs 2·155 grams; the molecular volume is 37·84 (Ramsay and Travers, Proc. Roy. Soc. 1901, 67, 329). At N. T. P. the refractive index of the gas for the green mercury line ($\lambda=5461$) is 1·0004287 (Cuthbertson and Cuthbertson, Proc. Roy. Soc. 1908, 81, A. 440; 1910, 84, A. 13). (For the viscosity of krypton *v.* Rankine, *ibid.* 1910, 83, A. 516; for its spectrum, *v.* Baly, Phil. Trans. 1903, 202, A. 183; Liveing and Dewar, Proc. Roy. Soc. 1901, 68, 389; Page, Proc. Physical Soc. 1912, 24, 138.)

Krypton is completely inactive, no compounds of the element being known. The gas is monatomic, since the ratio of its specific heats is 1·66 (Ramsay and Travers).

KUNKUR. An argillaceous limestone used in India for the preparation of mortar. It forms an excellent hydraulic mortar (E. Nicholson, Chem. News, 32, 82).

KUNZITE. A transparent, violet, or lilac-coloured variety of the mineral spodumene $LiAlSi_2O_6$ (*q.v.*), used as a gem-stone. It is found with pink tourmaline in the gem-mines of San Diego Co., California, and in Madagascar.

L. J. S.

KUPFERNICKEL *v.* NICCOLITE.

KUS-KUS ROOT. The rhizome of *Andropogon squarrosus* (Linn.), a marsh plant of the Gramineæ, growing in India, the Philippines, &c., and cultivated in Jamaica; gives an ethereal oil, *oleum æther vetiveriæ*, used in perfumery.

KUTEERA GUM *v.* GUMS.

KYANISING. A process for preserving timber, due to Kyan, of New York, in which a solution of mercuric chloride is forced into the pores of the wood.

KYANITE or **CYANITE.** (Fr. *Disthène.*) Aluminium silicate $Al_2O_3{\cdot}SiO_2$ or Al_2SiO_5, crystallised in the triclinic system. This compound is trimorphous and exists also as the minerals andalusite and sillimanite. Kyanite and andalusite are transformed at about 1300° into sillimanite, which melts at 1816°. Kyanite occurs as bundles of bladed crystals in mica-schist and gneiss, and is not an uncommon mineral. There is a perfect cleavage parallel to the flat of the blades, and one less perfect at the sides; whilst at ends there is a glide-plane which gives rise to very characteristic cross markings on the broad surface. The colour is usually pale blue, hence the name, from κυανός, blue. A remarkable feature is the difference in hardness (H. 4–7) on different faces and in different directions on the same face. Sp.gr. 3·6. The mineral is not attacked by acids. Kyanite is occasionally used as a gem-stone. The best crystals come from Pizzo Forno, near Faido in Switzerland.

L. J. S.

KYANOL. Runge's term for aniline.

KYLINDRITE *v.* CYLINDRITE.

KYNITE *v.* EXPLOSIVES.

KYNURENIC ACID. An acid isolated from the urine of the dog by Liebig. Probably identical with 4-hydroxy-quinoline-2-carboxylic acid (Homer). *Cf.* Besthorn, Ber. 1921, 54 [B], 1330.

KYNURIN. Trade name for *p*-hydroxy-quinoline.

KYROFIN. Trade name for a substituted anilide $C_2H_5O{\cdot}C_6H_4{\cdot}NH{\cdot}COCH_2OCH_3$. Used as an antipyretic.

END OF THE THIRD VOLUME.

A DICTIONARY
OF
APPLIED CHEMISTRY

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